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THE

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I.—*On Propione, the Ketone of Propionic Acid.*

By Reginald I. Morley, Esq.

The comparatively late discovery of propionic (metacetonic) acid and the great difficulty attending the preparation of this compound, have hitherto prevented a detailed study of its products of decomposition, interesting though they are as being derived from the first term of the series $C_nH_nO_4$, in which the character of the fatty acids is clearly and definitely pronounced. The elegant method of preparing this acid which we possess, since a passage has been opened from the alcohols to the acids containing C_2H_2 additional, and placed one step higher in the system, will doubtless greatly assist in filling up the gap still existing in the history of these substances.

The following pages contain some remarks respecting a member of the propionic family, which if prepared at all, has not hitherto been directly derived from propionic acid; namely, propione, the homologue of acetone.

Almost ten years before Gottlieb* discovered propionic acid, Frémy,† in studying the action of hydrate of lime upon sugar, starch and gum, obtained, together with other products, an oily liquid, the analysis of which led him to the formula

$$C_6H_5O = 2 \text{ vols. of vapour,}$$

* Ann. Ch. Pharm. LII, 121.

† Ann. Ch. Phys. [2] LIX. 6.

and for which, on account of a certain analogy it exhibited with acetone, he adopted the name of metacetone. When Gottlieb found propionic acid, the assumption of a close relation of this acid with Frémy's metacetone was at once suggested, both by a comparison of the formulæ,

C_6H_5O Metacetone,
$HO, C_6H_5O_4$ Propionic acid,

and by the analogy of the processes giving rise to the formation of the two substances, the latter being produced by the action of hydrate of potassa upon cane-sugar.

Induced by the relations exhibited by the above formulæ, Gottlieb examined the deportment of metacetone with oxidising agents, and found that it readily yielded the acid $C_6H_6O_4$, together with acetic and carbonic acids, and that the action of bichromate of potassa and sulphuric acid upon metacetone was actually the better process for preparing the acid, to which he accordingly applied the unfortunate term metacetonic or metacetic acid, only lately replaced by the more appropriate appellation of propionic acid, now universally adopted.

More recently, Chancel,* in his valuable researches into the nature of the ketones generally, was led to doubt the accuracy of Frémy's analysis, performed at a comparatively early period of the development of organic chemistry. He suggested that Frémy's metacetone might be the true ketone of propionic acid represented either by

C_5H_5O=2 vols. of vapour,

or, in the sense of his mode of viewing the substances,† by

$C_{10}H_{10}O_2$=4 vols of vapour,

and he supported this opinion chiefly, by Gottlieb's observation of metacetone being converted by the action of oxidising agents into propionic, acetic and carbonic acids, as stated above; a deportment assimilating this substance to acetone, which, as is well known, by similar treatment, yields acetic, formic and carbonic acids.

If we consider the difficulty attending the purification of substances produced in irregular processes of destructive distillation, a difficulty not undervalued by Frémy himself, and to which attention has again been directed by subsequent experiments of Chancel,‡ we cannot

* Compt. Rend. XX, 1882; XXI, 908.

† Compare Brazier and Gossleth's paper upon caproic and œnanthylic acids, Chem. Soc. Qu. J. III, 210.

‡ J. Pharm. XIII, 471.

but admit that the above suggestion has in itself a certain probability. On the other hand, it becomes again doubtful, if we consider the discrepancy between the boiling-point observed (84° C.) and that assigned to it by theory (100° C.), a fact to which Messrs. Brazier and Gossleth* have first directed attention. If we compare the widely differing percentages corresponding to both formulæ:

	Frémy's formula	Chancel's formula.
	C_6H_5O	C_5H_5O
Carbon	73·47	69·76
Hydrogen	10·20	11·62
Oxygen	16·33	18·62

and particularly if we consider that M. Cahours,† whose analytical skill and accuracy are universally appreciated, in his late researches on the volatile oils obtained in the distillation of wood, has met with a compound possessing exactly the composition and properties of Frémy's metacetone.

These statements suffice to show that the history of metacetone is still involved in obscurity, and that further researches are required in order to show whether Frémy's metacetone is merely a mixture containing propione as one of its constituents, or whether it be a definite compound, closely allied to, but differing in composition from the true propione.

To assist in clearing up this question, Dr. Hofmann induced me to try the preparation of propione by a method which was likely to yield this compound in a state of purity, namely by subjecting propionate of baryta to the action of heat.

The propionic acid used for this purpose was prepared by the process of Frankland and Kolbe,‡ with the slight modifications pointed out by Messrs. Brazier and Gossleth§ for the preparation of caproic acid.

I have only to mention that the decomposition which takes place in the preparation of the cyanide of ethyl by distilling the sulphovinate of potassa with cyanide of potassium (the second step in the process) is by no means confined to the production of cyanide of ethyl and sulphate of potassa, as vapours having the most intolerable odour are evolved during the whole operation, and the condensing-tube is lined with a light-yellow amorphous mass, evolving the odour of cyanic acid when treated with hydrochloric acid.

* Chem. Soc. Qu. J. III, 224.
† Chem. Soc. Qu. J. III, 183.
‡ Chem. Soc. Mem. III, 388.
§ Chem Soc. Qu. J. III, 210.

The propionate of potassa formed by boiling the cyanide of ethyl with an alcoholic solution of potassa, was decomposed by sulphuric acid and subjected to distillation, when the propionic acid passed over and collected in the receiver as an oily layer, not miscible with a small quantity of water, but disappearing upon considerable dilution. The odour of this substance is hardly to be distinguished from acetic acid, and with sesquichloride of iron it yields the characteristic red colour of the latter.

In order to identify the acid, a portion was converted into the ammonia-salt and subsequently into the silver-salt; the latter was white, crystalline, tolerably soluble in cold, and much more so, but with decomposition, in boiling water. On analysis:

5·06 grains of silver-salt gave
3·03 „ „ silver = 59·88 per cent.

The formula $Ag . C_6H_5O_4$ requires 59·66 per cent of silver.

The purity of the acid having thus been established, the rest was converted into a baryta-salt by saturation with the carbonate, and evaporation. This salt crystallises very beautifully, and justifies the name of propionic acid by its somewhat greasy appearance; when dried in the water-bath, it may be easily reduced to powder.

When submitted to destructive distillation (which is conveniently performed in Florence flasks placed obliquely upon a wire gauze over a gas-burner), a brown fluid, of not unpleasant odour, distilled over; when dehydrated with chloride of calcium and again rectified, it came over of a light-yellow colour. Thus purified, the fluid began to boil at 80° C., but the boiling-point rapidly rose to 100° C., between which temperatures a very small portion passed over, the last drops having distilled before the thermometer reached 108° C. On rectifying the fraction which distilled from 100° C. to 105° C., it began to boil at 98° C.; at 100° C. a constant boiling-point was observed.

Combustion of the product, collected at 100° with protoxide of copper and oxidised copper turnings, gave the following results:

I. 3·08 grains of substance gave
7·82 „ „ carbonic acid,
3·32 „ „ water.
II. 2·78 „ „ substance gave
7·08 „ „ carbonic acid,
2·93 „ „ water.

These numbers lead to the formula :

$C_5 H_5 O$ =2 vols. of vapour,
or, $C_{10}H_{10}O_2$=4 vols. of vapour,

which require the following values :

	Theory.		Mean of experiments.
5 equivs. of Carbon . .	30	= 69·76	69·34
5 „ „ Hydrogen .	5	= 11·62	11·83
1 „ „ Oxygen . .	8	= 18·62	
	43	100·00	

The body then produced by the distillation of propionate of baryta is the true propione, whose formation is analogous to that of acetone, as exhibited in the following equation :

$$\underbrace{Ba\,C_6H_5O_4}_{\text{Propionate of baryta.}} = \underbrace{C_5H_5O}_{\text{Propione.}} + Ba\,CO_3.$$

When pure, propione is a colourless or pale-yellow liquid, of an agreeable odour, and lighter than water, with which it is not miscible; the latter property distinguishes this compound essentially from acetone, and characterises it in an unequivocal manner as a derivative of a fatty acid. Propione is miscible in all proportions with alcohol and ether. It is very inflammable, and burns with a pale-blue flame without deposition of carbon.

The boiling-point of this liquid is not less than 16° higher than that observed by Frémy in metacetone, and is particularly interesting, inasmuch as it exactly corresponds with the temperature assigned by theoretical speculation. Propione being the intermediate term between the ketones of acetic and butyric acids, we are naturally led to assume, that its boiling-point should be equidistant from those of its neighbours in the system; now this is actually the case, as seen from the comparison appended.

		Boiling-points.	
Acetone . .	C_3H_3O	56° C.	diff. 44.
Propione . .	C_5H_5O	100° C.	
Butyrone . .	C_7H_7O	144° C.	diff. 44.

Moreover, if we adopt formulæ representing 4 vols. of vapour, the differences of the boiling-points closely approximate to the differences usually observed in bodies whose compositions differ by C_2H_2.

		Boiling-points.	
Acetone . .	$C_6H_6O_2$	56° C.	$C_4H_4=2C_2H_2$ $44=2\times22$
Propione . .	$C_{10}H_{10}O_2$	100° C.	
Butyrone . .	$C_{14}H_{14}O_2$	144° C.	$C_4H_4=2C_2H_2$ $44=2\times22$

It now remained only to study the deportment of propione with oxidising agents, in order to obtain new data for or against Chancel's opinion respecting the constitution of the ketones, for a full explanation of which I refer to the paper of Messrs. Brazier and Gossleth. According to this view, propione would be

$$C_{10}H_{10}O_2=C_6H_6O_2+C_4H_4,$$

and should yield on oxidation propionic and acetic acids.

ACTION OF NITRIC ACID ON PROPIONE.

Propione, when dropped by small portions into fuming nitric acid, caused very violent evolution of red fumes; after all action had ceased, the liquid was mixed with an excess of water and distilled. A portion of the distillate neutralised with ammonia and precipitated with nitrate of silver, gave a yellowish crystalline salt, which was recrystallised from boiling water, when a small quantity of silver was found to separate. The solution deposited white crystals, which on analysis were proved to consist of propionate of silver.

5·31 grains of silver-salt gave
3·19 „ „ silver=60·07 per cent.

Theory requires 59·66 per cent of silver.

The action of boiling nitric acid was now tried, with precisely similar results. I have repeatedly endeavoured to ascertain the presence of other acids in addition to propionic acid in the distillate of propione with nitric acid, such as nitropropionic acid* or acetic acid, but I have not succeeded in establishing their presence by experiment. I cannot, however, positively affirm that no other than propionic acid is formed, my experiments being performed perhaps on too small a scale, only a limited quantity of substance being at my command.

If we assume that the oxidation of propione furnishes propionic

* Gmelin (Handbuch V, 130) states that Chancel has obtained nitropropionic acid by oxidising metacetone with nitric acid. But on carefully going over the original memoirs of Chancel, I find this fact nowhere mentioned; it seems that nitropropionic acid has hitherto been obtained only from butyrale and from butyrone.

acid only, the deportment of this substance differs from that both of its lower and higher homologues, acetone yielding, under the same circumstances, acetic, formic and carbonic acids, while butyrone and caprone are converted into the nitro-acid of the lower series, namely into nitropropionic and nitrovaleric acids. If we leave out of consideration for the present Chancel's view regarding the constitution of ketones, which evidently requires further elaboration, it nevertheless appears that the fact of propione being reconvertible into propionic acid, together with the boiling-point of this substance differing 44° from those both of its lower and higher homologues, are in favour of the assumption, at all events, of formulæ corresponding to 4 vols. of vapour.

Among the series of ketones which are becoming more and more complete, there is one most interesting term still wanting, the study of which might probably decide the value of Chancel's view; this is the ketone of formic acid, which, according to his theory, should be identical with the aldehyde of the formyl-series. I am now engaged in preparing a considerable quantity of formic acid to be devoted to this investigation, and hope before long to lay the result of my labours before the Society.

II.—*Analysis of the Water of the Artesian Well, Southampton.*

By Joshua H. Robson, Esq.,

QUEENWOOD COLLEGE.

The few analyses of deep well-water which have hitherto been published exhibit a very great difference in the quantity of their solid matter, and even the quality of the water appears to be subject to much variation.* Professor Brande is inclined to believe that the quantity of solid matter depends upon the depth to which the borings have been carried in the chalk; he considers that the greater the depth the less will be the solid contents of the water.

From these considerations I was induced, at the suggestion of Mr. Galloway, to submit to analysis the Southampton artesian well-water, as, from the great depth to which the borings have been carried in this case, it was likely to yield some interesting results.

* *Vide* Messrs. Abel and Rowney's Memoir on the Composition of Water of the Artesian Wells, Quarterly Journal of the Chemical Society, Vol. I.; and Professor Brande's Paper on the Well-water of the Royal Mint, Vol. II. of the same Journal.

The analysis was conducted in the laboratory attached to this institution.

This well is situated on a common, about a mile and a half from the town of Southampton, and has cost in its construction between £20,000 and £30,000. The total depth is about 1280 feet; the depth from the surface down to the chalk is about 580 feet, and the depth of the borings in the chalk about 700 feet. It yields a mean supply of 125,000 gallons of water per diem, which is pumped up by means of two pumps, and delivered into a reservoir about an acre in extent.

The temperature of the water is 63° F. (31° C.), the temperature of the air being 57° F. (28° C.) at the time of observation. Its specific gravity is 1002·23; its reaction, acid. A careful qualitative analysis of the water having pointed out the presence of soda, magnesia, iron, sulphuric, silicic, carbonic, and hydrochloric acids, and traces of phosphoric acid and potash, the following numbers were obtained by quantitative analysis.

A. Determination of the total amount of fixed ingredients.

	Amount of water.	Fixed residue.	Percentage.
I.	566·9367 grms.	·7404 grm.	·13060
II.	566·9367 „	·7365 „	·12990
		Mean	·13025

B. Determination of sulphuric acid.

	Amount of water.	Amount of sulphate of baryta.	Sulphuric acid per cent.
I.	566·9367 grms.	·0564 grm.	·00340
II.	566·9367 „	·0561 „	·00339
		Mean	·00339

C. Determination of chlorine.

	Amount of water.	Amount of chloride of silver.	Chlorine per cent.
I.	566·9367 grms.	1·3941 grm.	·06083
II.	566·9367 „	1·3525 „	·05902
		Mean	·05992

D. Determination of silicic acid.

Amount of water.	Amount of silicic acid.	Silicic acid per cent.
I. 1133·8734 grms.	·0135 grm.	·00119
II. 1133·8734 „	·0168 „	·00148
	Mean	·00133

E. a. Determination of the total amount of iron.

Amount of water.	Amount of peroxide of iron.	Peroxide of iron per cent.
I. 1133·8734 grms.	·0046 grm.	·000405
II. 1133·8734 „	·0456 „	·000490
	Mean	·000447

F. a. Determination of the total amount of lime.

Amount of water.	Amount of carbonate of lime.	Lime per cent.
I. 1133·8734 grms.	·1792 grm.	·00885
II. 1133·8734 „	·1790 „	.00882
	Mean	·00883

G. a. Determination of the total amount of magnesia.

Amount of water.	Amount of pyrophosphate of magnesia.	Magnesia per cent.
I. 1133·8734 grms.	·1985 grm.	·00638
II. 1133·8734 „	·1922 „	·00618
	Mean	·00628

A given quantity of the water was boiled for a considerable time, the apparatus in which the operation was performed being so arranged that no evaporation could take place. The precipitate formed was separated by filtration, and the amount of iron, lime, and magnesia present in the precipitate, and the lime and magnesia present in the filtration, were determined in the usual way. All the iron was precipitated on boiling the water.

E. b. Determination of iron in the precipitate.

Amount of water.	Amount of peroxide of iron.	Peroxide of iron per cent.
1133·8734 grms.	·00460 grm.	·000405

Mean of the results ·00043 per cent, corresponding to ·00062 per cent of carbonate of the protoxide of iron.

F. b. Determination of lime in the precipitate.

	Amount of water.	Amount of carbonate of lime.	Lime per cent.
I.	1133·8734 grms.	·1113 grm.	·00549
II.	1133·8734 „	·1183 „	·00583
		Mean	·00566

c. Determination of lime in the filtrate.

	Amount of water.	Amount of carbonate of lime.	Lime per cent.
I.	1133·8734 grms.	·0724 grm.	·00353
II.	1133·8734 „	·0650 „	·00321
		Mean	·00337

G. b. Determination of magnesia in the precipitate.

	Amount of water.	Amount of pyrophospate of magnesia.	Magnesia per cent.
I.	1133·8734 grms.	·0723 grm.	·00232
II.	1133·8734 „	·0876 „	·00281
		Mean	·00256

c. Determination of magnesia in the filtrate.

	Amount of water.	Amount of pyrophoshate of magnesia.	Magnesia per cent.
I.	1133·8734 grms.	·1088 grm.	·00350
II.	1133·8734 „	·1068 „	·00343
		Mean	·00346

·00346 per cent of magnesia corresponds to ·00212 of magnesium.

H. Determination of the alkalis.

	Amount of water.	Amount of the mixed chlorides.	Mixed chlorides per cent.
I.	1133·8734 grms.	1·0650 grms.	·09354
II.	1133·8734 „	1·0455 „	·09920
		Mean	·09287

a. Determination of potash.

	Amount of water.	Amount of chloride of potassium and platinum.	Chloride of potassium per cent.
I.	1133·8734 grms.	·1205 grm.	·00324
II.	1133·8734 „	·1280 „	·00344
			Mean ·00334

·00334 per cent of chloride of potassium corresponds to ·00211 of potash.

b. Determination of chloride of sodium.

	Amount of water.	Amount of chloride of sodium.	Chloride of sodium per cent.
I.	1133·8734 grms.	1·02824 grms.	·09068
II.	1133·8734 „	1·00646 „	·08876
			Mean ·08972

·08972 per cent of chloride of sodium corresponds to ·03524 of sodium.

I. Determination of carbonic acid.

The carbonic acid was determined by adding to a known quantity of water a mixture of chloride of calcium and ammonia. 2267·7468 grms. of water yielded in this manner 1·4143 grms. of precipitate, in which the carbonic acid was determined.

	Amount of precipitate employed.	Amount of carbonic acid evolved.	Amount calculated on the whole precipitate.
I.	·5488 grm.	·2144 grm.	·55252
II.	·6429 „	·2730 „	·60056
			Mean ·57654

Percentage in the water ·02542.

K. Determination of phosphoric acid.

Amount of water.	Amount of pyrophosphate of magnesia.	Phosphoric acid per cent.
3401·6202 grms.	·0309 grm.	·000576

L. Determination of organic matter.

	Amount of water.	Amount of organic matter.	Organic matter per cent.
I.	1133·8734 grms.	·0790 grm.	·00697
II.	1133·8734 „	·0803 „	·00704
			Mean ·00700

From these analytical results, the following composition of the water is deduced:

	In 100 litres. Grammes.	In the imperial gallon. Grains.
Carbonate of protoxide of iron	·620	·4340
Carbonate of lime	13·740	9·6180
Carbonate of magnesia	5·280	3·6960
Phosphate of lime	1·248	·8736
Sulphate of lime	4·370	3·0590
Chloride of magnesium	3·680	2·5760
Sulphate of potash	3·910	2·7370
Chloride of sodium	89·720	62·8040
Silica	1·330	·9310
Organic matter	7·000	4·9000
	130·898	91·6286

The amount of fixed residue obtained by direct experiment was

In 100 litres . . . . . 130·250 grammes.
In the imperial gallon . . 91·175 grains.

Having deducted from the percentage of carbonic acid that portion in combination with lime, magnesia and iron, the percentage of free carbonic acid was found to be ·01643.

III.—*On the Selenocyanides.*

By William Crookes, Esq.,

assistant in the royal college of chemistry.

The remarkable parallelism between sulphur and selenium, which has been traced in so many directions, left but little doubt respecting the existence in the selenium-series of a class of compounds corresponding to the sulphocyanides. In fact, Berzelius* mentions, that by fusing selenium with ferrocyanide of potassium, a salt may be obtained which possesses the general characters of the sulphocyanide of potassium, but is less stable than the latter compound. This salt, however, appears to have hitherto escaped a closer examination. Berzelius makes no mention that it has ever been analysed, nor have any other selenocyanides been investigated.

* Traité, III, 105.

This circumstance induced me to re-prepare the potassium-salt, in order to fix its composition by numbers, and to study at the same time several other selenocyanides, in order to establish more fully the character of this class of compounds.

I begin the account of my experiments with a detailed description of both the preparation and analysis of the potassium-salt, which forms the point of departure of the investigation.

Selenocyanide of Potassium.—This salt was prepared by fusing 1 part of selenium with 3 parts of dry ferrocyanide of potassium in a small German glass retort. The greenish-black deliquescent mass was quickly broken up, and introduced into absolute alcohol. After digesting for a few days, the mixture was filtered; the residue, consisting chiefly of carbide of iron with a little selenide, was well washed with absolute alcohol, and the filtrate subjected to a stream of dry carbonic acid, in order to convert the soluble cyanide of potassium and cyanate of potassa into bicarbonate, which is insoluble in absolute alcohol.*

After filtration, the alcohol was distilled off, together with the hydrocyanic and cyanic acids, and their products of decomposition; the residue, which contained a small quantity of free selenium, was then treated with water, and the extract evaporated over sulphuric acid *in vacuo*.

Selenocyanide of potassium forms a mass of needle-shaped crystals, much resembling the corresponding sulphocyanide, very deliquescent, and decomposed by almost any acid, with evolution of hydrocyanic acid and precipitation of selenium. It is strongly alkaline to test paper, and produces great decrease of temperature when dissolved in water. When heated in a close vessel, it fuses, without decomposition, into a clear liquid below a red-heat, solidifying on cooling as a mass of crystalline structure: with access of air, however, it is decomposed a little above 100° C.

The potassium was determined by heating with dilute hydrochloric acid, evaporating the filtrate to dryness, heating to dull redness, and weighing the chloride of potassium produced. The selenium was at first determined by precipitating the solution of the salt with hydrochloric acid; but as this method did not give the whole of the selenium, a portion of it escaping in the form of hydroselenic acid, I

* In order to ascertain whether the decomposition of the cyanide of potassium by carbonic acid was complete, I dissolved half a gramme of cyanide, containing a little cyanate, in absolute alcohol, and passed a rapid stream of dry carbonic acid through the solution for about an hour. There was an abundant deposit of bicarbonate of potassa, and the filtrate, when evaporated to dryness, left a very slight residue, which entirely disappeared below a red-heat.

afterwards fused the potassium-salt with an excess of nitre, and estimated the selenium as seleniate of baryta.

When heated with dilute hydrochloric acid:

I. 0·3625 grm. of selenocyanide of potassium, dried at 100° C., gave
0·187 „ „ chloride of potassium, and
0·198 „ „ selenium.

When fused with nitre,

II. 0·4255 grm. of salt gave
0·8276 „ „ seleniate of baryta,

which correspond to the following percentages:

	I.	II.
Potassium . . .	27·00	—
Selenium . . .	54·62	54·88

These numbers lead to the formula

$$K C_2 N Se_2 = K Csey,$$

as may be seen by the following table:

	Theory.		Mean of experiments.
1 equiv. of Potassium . .	39·00	27·05	27·00
1 „ „ Cyanogen . .	26·00	18·05	—
2 „ „ Selenium . .	79·14	54·90	54·75
1 equiv. of K Csey . . .	144·14	100·00	

The formation of selenocyanide of potassium in the fusion of ferrocyanide of potassium with selenium is represented by the following equation:

$$K_2 Cfy + 4 Se = 2KC_2 N Se_2 + Fe C_2 + N.$$

I have examined the residue left in the retort, which, together with undecomposed ferrocyanide of potassium, consists chiefly of carbide of iron, retaining only traces of selenium. Berzelius* mentions that the nitrogen evolved during the process is mixed with the vapour of selenide of carbon. The formation of this latter compound must have been evidently due to the action of an excess of selenium upon the residuary carbide of iron, both constituents of which may have been converted into selenides at a high temperature. The gas evolved in my experiments did not contain any biselenide of carbon, at least

* Traité, III, 105.

I did not succeed in condensing any; nor is it likely that this compound could have been formed, as, from reasons of economy, I invariably used a large excess of ferrocyanide of potassium in proportion to the selenium employed.

The above equation requires 1·16 of ferrocyanide of potassium to 1 part of selenium. As stated above, I fused the two substances in the proportion of 3 to 1.

Selenocyanide of Silver.—This salt falls down when selenocyanide of potassium is added to a solution of nitrate of silver. Prepared in this manner it resembles chloride of silver in outward appearance. It may be obtained beautifully crystalline, however, by previously adding an excess of ammonia to the silver-solution; in this way it is precipitated in minute crystals, having exactly the appearance of satin. It blackens readily in the light, is insoluble in water, and almost so in ammonia and cold dilute acids; when boiled in strong acids it is immediately decomposed, and unless oxidising acids are employed, selenium is precipitated.

The silver in this salt was determined by heating with hydrochloric acid containing a few drops of nitric acid, and weighing the resulting chloride; the filtrate served to estimate the selenium which was precipitated by sulphurous acid and ammonia.

Treated in this manner

I. 0·3172 grm. of silver-salt, dried at 100° C., gave
0·2115 „ „ chloride of silver.
II. 0·4464 „ „ silver-salt, gave
0·2985 „ „ chloride of silver, and
0·1656 „ „ selenium,

corresponding to the following percentages:

	I.	II.
Silver . . .	50·18	50·31
Selenium . .	—	37·09

and leading to the formula

$$Ag\,C_2\,NSe_2 = Ag\,Csey.$$

as the following table shows:

	Theory.		Mean of experiments.
1 equiv. of Silver . . .	108·00	50·06	50·24
1 „ „ Cyanogen . .	26·00	12·8	—
2 „ „ Selenium . .	79·14	37·13	37·09
1 „ „ Silver-salt . .	213·14	100·00	

Selenocyanide of Lead.—On adding acetate of lead to a solution of selenocyanide of potassium, a lemon-yellow compound is precipitated. It is soluble in boiling water, but is slightly decomposed; the filtered solution, which is neutral to test paper, deposits, on cooling, beautiful lemon-coloured needles, which are insoluble in alcohol. The salt may be exposed without decomposition to a temperature of 100° C., but assumes when moist a slight pink tint. The crystals are extremely light.

The lead was determined by heating a portion of the salt in a crucible with strong sulphuric acid, which converts it entirely into sulphate. The carbon was determined in the usual manner.

I. 0·1735 grm. of selenocyanide of lead, dried at 100°, gave
0·125 „ „ sulphate of lead.
II. 0·6235 „ „ salt, burnt with protoxide of copper, gave
0·1309 „ „ carbonic acid.

Centesimally,

	I.	II.
Lead . . .	49·22	—
Carbon . .	—	5·72

The formula

$$Pb\,C_2\,N\,Se_2 = Pb\,Csey$$

requires the following values:

	Theory.		Experiment.
1 equiv. of Lead . . .	103·56	49·62	49·22
2 „ „ Selenium . .	79·14	37·92	—
2 „ „ Carbon . .	12·00	5·75	5·72
1 „ „ Nitrogen . .	14·00	6·71	—
1 „ „ Lead-salt . .	208·70	100·00	

Selenocyanide of Mercury with Protochloride of Mercury.—This beautiful compound is obtained by adding an excess of protochloride of mercury to selenocyanide of potassium; when concentrated solutions are employed, the whole immediately solidifies into a felt-like mass of yellowish crystals; these, when washed with cold water, are purified by crystallisation from alcohol. The crystals of this double salt are sparingly soluble in cold water, rather more so in hot, and very soluble in alcohol and dilute hydrochloric acid; it does not seem, however, to dissolve in the latter without decomposition, as the solution deposits selenium after standing for some time; nitric and nitrohydrochloric

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acids dissolve it entirely, the liberated selenium being immediately oxidized. The crystals are anhydrous, and may be heated to 100° C. without decomposition; they are decomposed a little above that temperature, intumescing in a remarkable manner.

The mercury was determined by dissolving the salt in hot dilute hydrochloric acid, and precipitating that metal in the filtrate by hydrosulphuric acid. The chlorine was estimated by dissolving in strong nitric acid, and adding nitrate of silver. I also determined the chlorine and selenium in the same portion by fusing a certain quantity with nitre and carbonate of soda, precipitating the chlorine with nitrate of silver, removing the excess of silver with hydrochloric acid, and precipitating the selenic acid by means of chloride of barium.

I. 0·259 grm. of salt dried at 100° C. yielded
0·1755 „ „ protosulphide of mercury.
II. 0·4673 „ „ double salt, yielded
0·3173 „ „ protosulphide of mercury.
III. 0·5625 „ „ salt, gave
0·2364 „ „ chloride of silver, and
0·477 „ „ seleniate of baryta.
IV. 0·4425 „ „ salt, gave
0·1855 „ „ chloride of silver.

Percentage,

	I.	II.	III.	IV.
Mercury . .	58·41	58·53	—	—
Chlorine . .	—	—	10·38	10·37
Selenium . .	—	—	23·93	—

These numbers lead to the formula

$$Hg\,C_2\,NSe_2\,Hg\,Cl,$$

representing a compound of equal equivalents of selenocyanide of mercury and chloride of mercury, which requires the following values:

	Theory.		Mean of experiments.
2 equiv. of Mercury . .	200·00	58·71	58·47
1 „ „ Cyanogen . .	26·00	7·64	—
2 „ „ Selenium . .	79·14	23·23	23·93
1 „ „ Chlorine . .	35·50	10·42	10·38
1 „ „ Double salt .	340·64	100·00	

All my attempts to produce the simple selenocyanide of mercury

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have hitherto failed. In repeated operations I did not obtain anything except the double compound.

I was curious to ascertain whether sulphocyanide of potassium might exhibit a similar deportment with chloride of mercury. On adding the latter salt in excess to sulphocyanide of potassium, I obtained a voluminous precipitate of needle-shaped crystals, possessing about the same solubility in water, alcohol and dilute hydrochloric acid as the selenocyanide, but I was unable to detect a trace of chlorine in them, either before or after crystallisation from alcohol.

On analysis the following results were obtained:

I. 0·3685 grm. of substance, gave
0·2693 „ „ protosulphide of mercury.
II. 0·3877 „ „ salt, gave
0·2831 „ „ protosulphide of mercury.

Percentage:

	I.	II.
Mercury	62·99	62·93.

The formula

$$Hg\,C_2\,NS_2 = Hg\,Csy.$$

requires the following values:

	Theory.		Mean of experiments.
1 equiv. of Mercury . . .	100·00	63·29	62·96
1 „ „ Sulphocyanogen .	58·00	36·71	——
1 „ „ Mercury-salt . .	158·00	100·00	

These numbers show that the salt under examination was the simple sulphocyanide of mercury, which has not hitherto been analysed.

Hence sulphocyanide and selenocyanide of potassium exhibit a different behaviour with chloride of mercury.

Hydroselenocyanic Acid.—By suspending finely divided selenocyanide of lead in a warm aqueous solution of the same salt, and subjecting it to a rapid stream of hydrosulphuric acid gas, hydroselenocyanic acid is obtained in solution; the liquid filtered off from the sulphide of lead must be heated to near its boiling-point to expel the excess of hydrosulphuric acid, and again filtered from a small quantity of precipitated selenium. Thus prepared, it is a very acid liquid, easily decomposed by boiling, or exposure to the air; it cannot be concentrated, even over sulphuric acid in vacuo, without

decomposition: the addition of almost any acid causes an immediate precipitate of selenium, hydrocyanic acid remaining in solution. It dissolves iron and zinc with evolution of hydrogen, and displaces carbonic acid from the carbonates. All its salts may be formed from it by direct combination.

The free acid existing only in solution, an analysis became impossible; however, the composition of the preceding compounds, and the analogy of hydrosulphocyanic acid warrant the assumption of the formula,

$$H C_2 N Se_2 = H Csey,$$

and hence we have the following series:

Hydroselenocyanic acid . . .	H Csey.
Potassium-salt	K Csey.
Silver-salt	Ag Csey.
Lead-salt	Pb Csey.
Mercury double-salt	Hg Csey + Hg Cl.

The following salts I have only examined qualitatively.

Selenocyanide of Sodium, prepared by neutralising the free acid, is alkaline, and very soluble; it crystallises in vacuo in small foliated crystals.

Selenocyanide of Ammonium, prepared in the same manner, is deposited in minute needles, very similar to those of the potassium-salt; it is extremely deliquescent.

Selenocyanide of Barium.—This salt was obtained by dissolving carbonate of baryta in the acid, and evaporating over sulphuric acid in vacuo. I could not obtain it in any definite crystalline form.

Selenocyanide of Strontium, obtained like the barium-salt; it crystallises in well-defined prisms.

Selenocyanide of Calcium, obtained in the same manner as the two former, crystallises in groups of stellated needles.

Selenocyanide of Magnesium dries up into a gummy mass, apparently devoid of crystalline structure.

Selenocyanide of Zinc.—This salt may be obtained either by dissolving the metal or its oxide in hydroselenocyanic acid; it forms groups of prismatic needles, which are not deliquescent.

Selenocyanide of Iron.—Owing to the rapid decomposition of the salts of hydroselenocyanic acid when in contact with stronger acids, I was unable to obtain any coloration with salts of sesquioxide of iron by double decomposition. I was also unsuccessful in preparing

it by treating sesquioxide of iron with hydroselenocyanic acid, selenium being immediately precipitated. The salt was, however, once obtained by accident; I was preparing some selenocyanide of potassium by igniting selenium with ferrocyanide of potassium; the result of the fusion was treated with absolute alcohol in a well-closed flask; on filtering off, I found the liquid to have a deep blood-red colour, which soon disappeared on exposure to the air, with deposition of selenium. I have not obtained any colour at other times, the iron always remaining behind as a black powder, chiefly containing carbide of iron.

Selenocyanide of Copper.—When selenocyanide of potassium is added to sulphate of copper, a brownish precipitate falls down, which is probably the selenocyanide. I was unable to obtain it in a state fit for analysis, as it rapidly decomposed, even at the common temperature, into black selenide of copper, with separation of hydroselenic acid.

I cannot conclude without acknowledging the great obligation I am under to Professor Hofmann, for placing at my disposal so large a quantity of selenium, and also for his valuable advice and assistance during the progress of these experiments.

IV.—*On the Composition of certain Well-waters in the neighbourhood of London, with some observations on their action on lead.*

By Henry M. Noad, Esq.,

lecturer on chemistry at st. george's hospital.

The mineral and organic constituents of the waters employed for domestic use in large towns have lately occupied a considerable share of public attention. It has been justly considered that the purity of this all-important fluid must exert great influence on general health, and with equal truth has it been surmised that waters having their origin in the immediate neighbourhood of crowded cities must contain ingredients incompatible with their use as a beverage and for other household purposes.

The mineral constituents of spring-waters usually take their character from the geological nature of the localities in which they originate. Speaking generally, they contain nothing objectionable; but should there be a predominance of any particular ingredient, or should the

amount of saline matter be considerable, a marked character is given to the water, which then receives the general name of "mineral." Such waters rarely require the assistance of the chemist to point out their unfitness for domestic use; they are distinguished either by a peculiar taste, or smell, or colour, or hardness, and are at once discarded.

The question, whether water for drinking should or should not contain mineral matter, is still a vexed one; and as it is one of medicine rather than of chemistry, it need not be discussed here. General experience would, however, seem to indicate that a certain amount of saline matter is not objectionable, since there are no spring-waters that do not contain some. In this, as in many other things, *taste* grows out of *habit*, and the fickleness of water-drinkers is well known. Those accustomed to the continued use of the purer kinds of water, recoil almost with disgust from the saliferous springs, while the drinkers of the latter object quite as strongly to the purer fluid, as being to their palates, flat, disagreeable, and almost nauseous.

But whatever may be thought of the mineral constituents, there can be but one opinion as to the influence of those organic impregnations so constantly met with in the waters of large towns. These consist, for the most part, of bodies in a state of progressive change or decomposition; and chemistry teaches us that such substances, when brought into contact with other organic substances, have a remarkable disposition to communicate to them their own molecular disquietude—to bring about organic decomposition. What diseases, then, may the continued use of such water engender? I believe, as I shall presently have occasion to show, that, in addition to its general unfitness for domestic use, water containing organic matter is particularly objectionable on account of its liability to become contaminated with *lead* when kept in cisterns of that metal; and that earthy and alkaline sulphates and chlorides, even when present in considerable quantity, do not in such waters act as preservatives.

Among the constituents of the well-waters of large towns, *nitric acid* has often been alluded to. Mere traces of it have, I believe, hitherto been found; at least I am not aware that a quantitative determination of it in any of the waters in or about the metropolis has hitherto been published. That it does, however, occasionally exist in large quantities, is shown by the following analysis by Mr. W. Fisher of a well-water from Highgate, one of a series of water-analyses that has for some time been in course of execution by the pupils in the laboratory of this medical school. Attention was directed to this water,

firstly, in consequence of its powerful action on the leaden cistern in which it was retained, and, *secondly*, on account of the unusual amount of saline matter which it contained. Its hardness has prevented its being much used for domestic purposes, which may probably be deemed a fortunate circumstance, as I have found the metal evidently acted upon after being immersed in a bottle of the water for a few days only. By the subjoined analysis, it will, I think, appear, that the remarkable action of this water on lead is referable to the comparatively small quantities of sulphates and chlorides, and to the extraordinary amount of *nitrates* which it contains. The source of the latter is pretty clearly pointed out by the situation of the well, which is immediately contiguous to the old churchyard on the very top of Highgate Hill, the loose and sandy soil of which must be teeming with organic substances in all stages of decay, and which, therefore, are constantly furnishing ammonia, from the oxidation of which the nitric acid is in all probability derived. The putrefaction of animal matters, in contact with calcareous soils, is well known to produce nitrate of lime; and it was long ago shown by Glauber, that a vault, plastered over with a mixture of lime, wood, ashes, and cow-dung, soon became covered with efflorescent nitre. In the water in question, the nitric acid exists in combination with *lime* and *magnesia*, which earths would naturally have occurred in the form of carbonates, held in solution by carbonic acid. Not a trace of carbonate now exists; neither does the water contain any appreciable quality of organic matter, which has been destroyed by the powerful oxidising operations which are constantly going on in the contiguous soil. I have examined the water from six other wells, at various distances from the churchyard, but all coming within the range of the Bagshot sand formation: in each, nitric acid has been detected; though, from the great trouble attending the quantitative estimation of this substance, a complete analysis has as yet been made only of the one first referred to.

Now, though the presence of earthy nitrates does not perhaps communicate any injurious or unwholesome quality to a water—indeed from the entire absence of decomposing organic substances it may be less objectionable as a beverage than the average waters of large cities—it is nevertheless important to bear in mind the powerful action of such waters on lead, and the possibility of its becoming the vehicle through which this subtle poison may be introduced into the system. The public, indeed, cannot be too emphatically warned against the too common practice of allowing *any* water intended

for domestic use to remain stored up in leaden vessels; for, as I shall have to show presently, the existence in the water of considerable quantities of both sulphates and chlorides is not always a security against saturnine impregnation.

The nitric acid in the Highgate water was estimated by the following process.

An imperial gallon was concentrated by evaporation to about half a pint, which was macerated with excess of recently prepared sulphate of silver, and allowed to remain at rest for twenty-four hours. It was then filtered; rendered alkaline by carbonate of soda; again filtered; and the filtrate concentrated by evaporation and distilled in a large retort with chemically pure sulphuric acid, the distillate being collected in a receiver containing strong baryta-water. The distillation was continued till fumes of sulphuric acid began to appear; it was then stopped and the retort allowed to cool; a quantity of distilled water was then added; and the distillation resumed and continued as before till fumes of sulphuric acid began to rise. This operation was repeated *thrice*, preliminary experiments having shown that the last portions of nitric acid are only expelled from the sulphuric acid residue, by thus urging them forward in an atmosphere of steam. The contents of the receiver, containing nitrate of baryta and excess of baryta-water, were exposed to the air in a large dish for twenty-four hours—then filtered—and into the clear filtrate a slow stream of carbonic acid gas was passed, till the liquor was no longer alkaline to test paper; it was next evaporated to dryness, and the residue treated with successive portions of boiling water till the whole of the nitrate of baryta was dissolved out. The clear solution being precipitated with sulphuric acid gave the amount of sulphate of baryta corresponding to that of the nitrate, and from which the amount of nitric acid was calculated. From the first experiment, made on water taken from the well in June, 1850, 76·75 grs. BaO. SO_3 = 85·96 BaO. NO_5 = 35·53 grs. NO_5, were obtained. From the second, made on water taken from the well in October, there were obtained from 28,000 grs. of the water, 33 grs. BaO. SO_3 = 37 grs. BaO. NO_5 = 15·29 grs. NO_5. The latter experiment gives 38 grs. of nitric acid in an imperial gallon of the water, a quantity rather larger than that obtained in the former experiment, in which traces of nitric acid were found in the sulphuric acid residue, even after three additions of water. In the second experiment, six additions of water were made, in quantities of about four ounces each time—the residue was now found entirely free from nitric acid.

Saline contents in the Imperial pint:

By direct estimation, 12·57 grains, consisting of:

Silica	0·1120 grs.
Sulphate of potash	2·1306 „
Sulphate of soda	1·1894 „
Chloride of sodium	1·2040 „
Chloride of calcium	0·7390 „
Nitrate of lime	5·0150 „
Nitrate of magnesia	2·1330 „
	12·5230

The next water to which I shall call the attention of the Society is from a spring at Clapham which was submitted to me for analysis in the summer of 1848, in consequence of its strong action on lead. I collected the water myself on the spot, and on the same occasion was shown the cistern, which was then nearly full of water, the surface of which was covered with a thick greasy scum, which proved, on examination, to consist almost entirely of oxide of lead. I expected to find this water unusually pure; to my surprise, however, it contained nearly 78 grains of solid matter per imperial gallon, the composition of which was:

Silica.	0·24
Carbonate of lime	15·09
Carbonate of magnesia	13·97
Sulphate of lime	15·32
Sulphate of potassa	6·79
Sulphate of soda	10·77
Chloride of sodium	11·46
Organic matter	4·10
	77·74

Here then we have an instance of a water containing an abundance of so-called "preservative salts," corroding lead with remarkable energy.*

The oxide of lead could be skimmed from the surface of the water in abundance; but on testing the water beneath, taking care to avoid filtering, by which a very considerable quantity of the metal, even

* I was shown by the plumber a piece of the bottom of the cistern, which in the course of six months had been eaten into holes.

when in solution, may be removed, no signs of lead could be detected. To what are we to ascribe this remarkable action? I believe to the presence, in the water, of an unusually large quantity of organic matter. It was during the summer months that the corrosion of the cistern took place so rapidly. The organic matters would then be undergoing the most active decomposition, and carbonic acid being constantly evolved against the sides and bottom of the cistern, would enter into combination with the *surface*-oxide, and so form carbonate of lead. This is by no means the only instance I have met with, of water abounding in sulphates and chlorides acting strongly on lead, and in every case that I have yet examined, organic matter has been present in unusual quantity. It is worthy of remark, that no lead could be found in solution; whenever this does occur, in any but pure or alkaline water, the metal is probably taken up in the form of oxichloride. Carbonate of lead is wholly insoluble, even in water highly charged with carbonic acid. I mention this because an idea is very generally prevalent that carbonate of lead, like the carbonates of lime and magnesia, may be rendered soluble by taking up an extra atom of carbonic acid. I have made direct experiments which negative this assumption, and it has since been pointed out to me that the same had been previously done by Dr. Taylor. But water, though it cannot take up carbonate of lead in solution, may, by keeping it in mechanical suspension, be the means of introducing this dangerous form of saturnine poison into the system. The practice of filtering water preserved in leaden cisterns, and intended for domestic use, cannot, therefore, be too warmly recommended.

I wish, lastly, to say a few words on another class of waters which act strongly on lead, viz: the *artesian-well waters of the London basin*. These waters are, I believe, always alkaline; those which I have examined are remarkably free from organic matter, and as there is no deficiency of preservative salts, it is to their alkalinity that I am inclined to attribute the corrosive action which they exert on this metal. From several analyses of these waters, which have lately been made in this laboratory, I select two, one from the premises of the Lord Chief Baron at Hatton, which was examined by Mr. Henry Pollock, in consequence of the rapidity with which it corroded the leaden cistern; and the other from the Lunatic Asylum at Colney Hatch, which I analyzed at the request of Mr. Rotch, the Chairman of the Board of Governors of that institution, with the view of ascertaining its general fitness for the purposes of the asylum, before fresh expenses were incurred for conveying it to

different parts of the building. It is worthy of remark, that Mr. Pollock was able to detect lead in the clear water of the cistern, which I had been unable to do in the case of the Clapham water.

The analysis of these two artesian waters gave the following results per imperial gallon :

	Hatton.	Colney Hatch.
Carbonate of lime	2·120	6·500
Carbonate of magnesia	·880	1·320
Carbonate of soda	15·196	7·100
Sulphate of potash	traces	2·590
Sulphate of soda	10·456	5·770
Sulphate of lime	„	4·555
Chloride of magnesium	„	4·260
Chloride of sodium	9·288	„
Protocarbonate of iron	·480	„
Soluble organic matter	„	·470
Phosphate of lime	traces	traces
Silica	·050	·670
	38·470	33·235
Saline matter by direct estimation	38·6	32·97

Of the excellence of both these waters for domestic use the analyses bear ample testimony; but with the example of the Hatton water before me, I felt bound to warn the Governors of the Colney Hatch Asylum, against the use of lead, either for storing the water, or for distributing it. I found, however, on visiting the institution, that my warning was not required, that metal being almost entirely banished from every part of the building.

V.—*Observations upon the Deportment of Diplatosamine with Cyanogen.*

By G. B. Buckton, Esq., F.L.S.

The peculiar deportment exhibited by aniline, toluidine, and several other volatile organic bases, when exposed to the action of cyanogen, rendered it desirable to investigate the behaviour of some of the fixed bases in the same direction. At the request of Dr. Hofmann, and with his supervision, I have undertaken some experiments on this

subject, the results of which I beg to communicate to the Chemical Society.

The substance on which I have worked is the remarkable alkaloid discovered by Reiset, obtained by the action of ammonia upon the green salt of Magnus, long known under the name of Reiset's first platinum-base, for which, more recently, the shorter name of diplatosamine has been proposed.

On passing a stream of cyanogen through a moderately concentrated solution of diplatosamine, free from carbonic acid, the gas is slowly absorbed, and after some time a yellowish-white crystalline substance is deposited, which continues to form until the solution changes colour from the partial decomposition of the cyanogen, at which point it is desirable to suspend the operation.

This substance is soluble to a slight extent in cold, but much more readily in boiling water, from which it may be recrystallised without difficulty. It then appears as a mass of minute colourless crystals, which under the microscope exhibit the form of hexagonal plates, and frequently arrange themselves in regular stellar groups. It is, however, difficult to obtain them without a yellow tinge, from traces of decomposed cyanogen, which obstinately adhere even after three crystallisations. When heated in the air, the substance spontaneously takes fire, and smoulders like tinder, leaving as sole residue a light sponge of platinum. It freely evolves ammonia when heated in a dry test-tube; but the presence of cyanogen could not be detected by the usual test of potassa, proto-sesquioxide of iron and hydrochloric acid.

On analysis this substance gave the following numbers:

I. 0·3465 grm. of substance, dried at 100°, left on ignition
0·2410 „ „ platinum.
II. 0·4005 „ „ substance gave
0·2780 „ „ platinum.
III. 0·4588 „ „ substance, when burnt with soda-lime, yielded
1·4700 „ „ ammonio-chloride of platinum, equivalent to
0·0922 „ „ nitrogen.
IV. 0·3957 „ „ substance yielded
1·2775 „ „ ammonio-chloride of platinum, equal to
0·0801 „ „ nitrogen.

These numbers correspond to the following percentages:

	I.	II.	III.	IV.
Platinum . . .	69·55	69·41	—	—
Nitrogen . . .	—	—	20·09	20·24

and also to the formula

$$Pt\,NH_3\,Cy,$$

as is exhibited in the annexed table:

		Theory.		Experimental mean.
1 equiv.	of Platinum . . .	98·68	69·64	69·48
2 „	„ Nitrogen . . .	28·00	19·78	20·16
3 „	„ Hydrogen . . .	3·00	2·12	—
2 „	„ Carbon . . .	12·00	8·46	—
		141·68	100·00	

These analyses show that the action of cyanogen upon diplatosamine, far from being analogous to that on aniline, toluidine, &c., (which, as is well known, combine directly with the gas,) gives rise to the same compound which Reiset obtained by saturating the base with hydrocyanic acid, and which he considered as the cyanide of his second series, viz., as the hydrocyanate of platosamine, or as the cyanide of platosammonium.

$$\left.\begin{matrix}H_2\\Pt\end{matrix}\right\}N\,.\,HCy,\ \text{or}\ \left.\begin{matrix}H_3\\Pt\end{matrix}\right\}N\,.\,Cy.$$

I have carefully compared the substance prepared by the action of cyanogen, with that obtained by Reiset's method, and find them identical in all respects.

It may be mentioned here, that a very convenient method of obtaining the compound in considerable quantity, consists in adding cyanide of potassium to the chloride of diplatosammonium (the direct product of the action of an excess of ammonia upon protochloride of platinum). By this process the tedious operation of isolating the base is avoided; the precipitate requires only two or three crystallisations to remove the soluble chloride of potassium.

The formation of the cyanide by the action of cyanogen upon a solution of diplatosamine is readily intelligible.

The mother-liquor of the crystals was found to contain a considerable quantity of carbonate of ammonia, and, moreover, the carbonate of diplatosamine. This compound was identified by conversion into the sulphate and analysis of the latter.

It is evident that the first action consists in a decomposition of water, the elements of which unite with cyanogen, producing hydrocyanic and cyanic acids; the former giving rise to the crystalline cyanide, ammonia, and water,

$$PtH_6N_2O\,.\,HO + HCy = PtH_3N\,.\,Cy + NH_3 + 2\,HO;$$

the latter inducing the transient formation of cyanate of diplatosamine, which, by assimilation of the elements of water, is immediately converted into the carbonate of this alkaloid and carbonate of ammonia.

$$Pt\,H_6\,N_2\,O, Cy\,O + 4\,HO = Pt\,H_6\,N_2\,O, CO_2 + NH_4\,O\,CO_2.$$

As the general deportment of the salt, $Pt\,H_3\,N\,Cy$, seemed to be somewhat anomalous, and in many respects different from that of an ordinary cyanide (the usual tests failing altogether to indicate the presence of cyanogen), I have studied the behaviour of this compound with various reagents, in order if possible to obtain new data by which to elucidate its constitution. The cyanide in question is soluble in potassa without decomposition. It imitates in this respect the deportment of cyanide of silver. It is also soluble without change in hydrochloric acid, although the crystals deposited from the solution assume a somewhat different shape and a yellow colour.* It may be recrystallised without decomposition also from dilute sulphuric acid. Concentrated sulphuric and nitric acids, however, decompose it; but the products of these reactions have not been farther examined.

The action of nitrate of silver upon the cyanide is very remarkable, and appears to throw much light upon the true nature of this substance.

When nitrate of silver is added to an aqueous solution of the cyanogen-compound, a copious, white, and curdy precipitate immediately falls, in outward appearance resembling cyanide of silver, and, like the latter salt, soluble in ammonia. On evaporating the solution, filtered off from the precipitate at a gentle heat, a crop of beautiful crystals made their appearance, which lost their transparency on carrying the evaporation to dryness. On raising the temperature beyond this point, they suddenly took fire, and left a residue of pure platinum. In the conception of the substance being cyanide of platosammonium,

* The substances crystallised from potassa (I.) and from hydrochloric acid (II.) were identified by analysis.

I. 0·4065 grm. of substance gave
0·2830 „ „ platinum.
II. 0·4685 „ „ substance gave
0·3250 „ „ platinum.

The experimental and theoretical percentages are—

	Theory.	Experiment.		Mean of experiments.
		I.	II.	
Platinum . . .	69·64	69·61	69·37	69·49

I was inclined to consider these needles as the nitrate of platosamine, when the reactions would have been represented by the equation,

$$Pt\,H_3\,N\,.\,Cy + Ag\,NO_6 = Pt\,H_3\,N\,.\,NO_6 + Ag\,Cy.$$

In order to verify this equation, the needles were subjected to analysis, when the following results were obtained:

I. 0·5030 grm. of this salt gave
0·2525 „ „ platinum.
II. 0·3930 „ „ from another preparation
0·1960 „ „ platinum.

These numbers, far from agreeing with the formula of the nitrate of platosamine, exhibit on the contrary a close accordance with the theoretical values required by the composition of the nitrate of Reiset's first compound, as may be seen by the following comparison:

	Theory.		Experiment.	
	$Pt\,H_3\,N,\,NO_6$	$Pt\,H_6\,N_2\,NO_6$	I.	II.
Platinum .	55·53	50·68	50·19	49·87

As the determination of nitrogen in the nitrate presented some difficulties, to vary the analysis and furnish a means of corroboration, a solution of the cyanide was precipitated with sulphate of silver, the filtrate evaporated, and the platinum determined in the sulphate thus obtained—

0·4080 grm. of substance gave
0·2215 „ „ platinum.

This result perfectly corroborates the inference drawn from the former analysis, namely, that the action of nitrate of silver upon the cyanide under examination gives rise to the formation of a salt, not of platosamine, but of diplatosamine (Reiset's first base). For the sake of comparison I subjoin the theoretical percentage of the salt:

	Theory.	Experiment.
Platinum	54·61	54·22

The unexpected results obtained in the examination of the soluble compound produced by the action of the silver-salt upon the cyanide, compelled me more carefully to investigate the white precipitate, which hitherto I had regarded as cyanide of silver. I found at once that this precipitate is by no means cyanide of silver, but that it contains platinum as one of its constituents.

The quantitative analysis of this white compound presented, how-

ever, some difficulty, from the extreme tenacity with which the cyanogen holds the combined metals. No constant results could be obtained by fusing with carbonate of soda and potassa, ignition with soda lime, or the combined action of nitric acid and chlorate of potassa. The analysis, however, succeeded without difficulty, when the salt under examination was dissolved in strong ammonia, and immediately precipitated with sulphide of ammonium, when pure sulphide of silver is thrown down, the whole of the platinum remaining in solution. This solution, when evaporated, yielded at first beautiful iridescent crystals, which subsequently left pure metallic platinum on ignition.

In this manner the following results were obtained:

I. 0·6019 grm. of substance gave
0·2884 „ „ sulphide of silver, equal to
0·2511 „ „ metallic silver, and
0·2305 „ „ platinum.
II. 0·4555* „ „ substance gave
0·1745 „ „ platinum.

These numbers correspond to the following percentages:

	I.	II.
Platinum . . .	38·29	38·30
Silver	41·71	—

and prove that the white precipitate is nothing but platino-cyanide of silver,

$$Ag\ Pt\ Cy_2,$$

as is exhibited in the following comparison of the experimental results with the values required by theory.

	Theory.		Mean of experiments.
2 equiv. of Cyanogen . . .	52·00	20·15	—
1 „ „ Platinum	98·68	38·10	38·29
1 „ „ Silver	108·00	41·75	41·71
1 „ „ Platino-cyanide of silver	258·68	100·00	

This conclusion was fully borne out by the deportment of the silver-salt with reagents, when compared with that of the platino-cyanide, obtained by the usual method.

Detailing the analysis of this substance, I have mentioned that on treating the ammoniacal solution of the cyanide with hydrosulphuric

* The silver was lost.

acid, iridescent needles are obtained. These needles are the corresponding platino-cyanide of ammonium. A similar result was found when the silver-salt was treated with potassa, with which on ebullition it gave a heavy black precipitate containing all the silver, and a colourless solution which yielded long needles of a purple hue by reflected, and yellow by transmitted light. These crystals change to a deep yellow when heated, and then fuse to a mass of carbon and platinum. The aqueous solution of this compound gives first a bright orange precipitate with the nitrate of the suboxide of mercury, which speedily changes to a cobalt-blue on increasing the quantity of the mercury-salt. It need scarcely be mentioned that this deportment, in all respects, agrees with that of the platino-cyanide of potassium described by Gmelin, which moreover was satisfactorily proved by direct comparison of the two salts.

The formation of platino-cyanide of silver from the cyanide which forms the subject of the present communication, fully explains the simultaneous production of a salt of Reiset's first base. The reaction is expressed by the following equation:

$$2\,Pt\,H_3\,N\,.\,Cy + Ag\,NO_6 = Pt\,H_6\,N_2\,.\,NO_6 + Ag.\,PtCy_2.$$

To obtain a quantitative control of the correctness of this equation, a weighed portion of the cyanide was decomposed by nitrate of silver. The precipitated salt was carefully dried upon a weighed filter, and the quantity obtained compared with the amount required by theory.

I. 0·2398 grm. of salt produced
0·2175 „ „ platino-cyanide of silver.
II. 0·5935 „ „ another specimen gave
0·5425 „ „ platino-cyanide of silver.

The quantity required by theory, and obtained by experiment, reduced to 100 parts, is as follows:

Theory.	Experiment.	
	I.	II.
91·29	90·70	91·40

The facts observed in the study of the crystalline compound which is formed by the action of hydrocyanic acid, or cyanogen, upon the oxide of diplatosammonium, suggests a mode of viewing the constitution of this substance which is different from that hitherto adopted.

If, with M. Reiset, we consider this compound as the cyanide of platosammonium, we are forced to admit that this substance owes its origin to a very singular play of affinity, inasmuch as the influence of

hydrocyanic acid on the oxide of diplatosammonium gives rise to the cyanide of platosammonium, whilst on the other hand a metallic solution reconverts this compound into a salt of the original base.

It appeared much simpler to regard the compound in question as a salt of the base from which it is derived, viz., as a platino-cyanide of diplatosammonium, which is isomeric with the cyanide of platosammonium.

$$2\,Pt\,H_3\,N\,.\,Cy = Pt\,H_6\,N_2\,.\,PtCy_2.$$

This formula explains equally well the formation of the substance by the action of hydrocyanic acid upon the oxide of diplatosammonium:

$$2Pt\,H_6\,N_2\,O + 4\,H\,Cy = Pt\,H_6\,N_2\,.\,Pt\,Cy_2 + 2\,NH_4\,Cy + 2\,HO,$$

but the interpretation of its behaviour with silver-salts becomes infinitely simpler, as the whole change is reduced to a case of ordinary double decomposition.

$$\underbrace{Pt\,H_6\,N_2\,.\,Pt\,Cy_2}_{\text{Platino-cyanide of diplatosammonium}} + \underbrace{Ag\,NO_6}_{\text{Nitrate of silver.}} = \underbrace{Pt\,H_6\,N_2\,.\,NO_6}_{\text{Nitrate of diplatosammonium.}} + \underbrace{Ag\,Pt\,Cy_2.}_{\text{Platino-cyanide of silver.}}$$

To test the accuracy of this view experimentally, I prepared a quantity of hydroplatino-cyanic acid, by treating the mercury-salt with hydrosulphuric acid. On saturating this acid with the oxide of diplatosammonium, I obtained at once a colourless crystalline substance, which could not be distinguished from the cyanide previously described, either by appearance or behaviour with reagents.

The same salt may be more conveniently procured, by adding platino-cyanide of potassium to the chloride of diplatosammonium.

On recrystallising and drying at 100°,

0·2084 grm. of substance gave on ignition
0·1446 „ „ platinum,

in accordance with the formula

$$Pt\,H_6\,N_2,\,Pt\,Cy_2,$$

the calculated and experimental numbers in 100 parts being,

	Theory.	Experiment.
Platinum . . .	69·64	69·34

On reference to Reiset's excellent paper upon the platino-bases, it does not appear that he attempted the construction of the cyanide of platosammonium, by directly operating upon a salt of the correspond-

ing base, considering, doubtless, that the substance would prove itself identical with that previously described by him.

As a last step, it appeared desirable to try the preparation of the true cyanide of platosammonium, as it was not improbable that a compound might be thus obtained, similar in composition, but differing in its molecular arrangement, and consequently presenting some possible discrepancies in its chemical and physical properties.

Accordingly, I digested a few grammes of the chloride of platosammonium with an excess of cyanide of silver; the decanted liquid was found to yield, on concentration, fine and regular needles of a pale-yellow colour. These crystals proved to be much more soluble in water and ammonia, than the platino-cyanide of diplatosammonium, from which they also materially differed in their deportment with reagents.

0·4695 grm. of substance gave
0·3256 „ „ platinum,

which agrees with the formula

$$Pt\,H_3\,N,\,Cy,$$

the numerical percentages being

	Theory.	Experiment.
Platinum . . .	69·64	69·35

Hence, it is evident that there are two substances of the same composition, the one, by the mode of formation and behaviour with reagents, proved to be a salt of a platinum-base with a platinum-acid, (platino-cyanide of diplatosammonium), the other, as far as we can judge from the method of preparation, the true cyanide of platosammonium.

The latter substance appears to call for closer attention than I have been able to bestow upon it; but I hope at a future time to have the honour of laying the results of an extended examination before the Chemical Society.

VI.—*On the Explosive Compound usually denominated Iodide of Nitrogen.*

By J. H. Gladstone, Ph.D., F.C.S.

The following experiments were made last summer with a view to settle the real composition of the so-called "iodide of nitrogen." This substance resulting from the mutual action of iodine, and ammonia in

solution, has already been the subject of much investigation; and the study of its reactions by different chemists has led to four different formulæ being assigned to it. The extremely explosive character of the substance precludes the idea of analysing it in the usual manner, as it would be impossible to place a portion in the scale-pan of a balance with any safety after it had been dried. Indirect modes of analysis, by which the relative proportion of its constituent elements is determined, appear to be offered by various decompositions, which the black powder may be made to undergo. M. Bineau* alone, has studied any of these hitherto: and his experiments led him to assign to the so-called iodide of nitrogen the composition NHI_2. The quantitative results recorded below will test the truth of this formula.

The substance employed by me was always prepared by decomposing an alcoholic solution of iodine by means of ammonia in excess. The black powder thus formed was completely washed by suffusion with distilled water, and decantation. It was found, that during this reaction, an amount of iodide of ammonium is formed slightly exceeding half the amount of iodine employed: a mere trace of iodic acid is also produced. This fact is opposed to the formula NI assigned to the black powder by Mitscherlich; for

$$4\,NH_3 + 4\,I = NI + 3\,NH_4\,I;$$

in which case the iodide of ammonium obtained would be quite three-fourths of the iodine originally acted upon; but it decides nothing, as to whether 1, 2, or 3 atoms of hydrogen in the ammonia are substituted by iodine; for

$$\begin{aligned} 2\,I + 2\,NH_3 &= NH_4\,I + NH_2\,I \quad \text{(Millon)}. \\ 4\,I + 3\,NH_3 &= 2\,NH_4\,I + NHI_2 \quad \text{(Bineau)}. \\ 6\,I + 4\,NH_3 &= 3\,NH_4\,I + NI_3. \end{aligned}$$

The black powder suffers spontaneous decomposition in pure water. Bubbles of gas are slowly given off; iodine is set free; and the solution (which is acid to test paper) contains hydriodic and iodic acids, together with ammonia. In an attempt to make use of this decomposition as a means of analysis, the iodic acid was found to be to the hydriodic acid in the ratio of 1 atom to 8·44 atoms; but it is not likely that the two acids always maintain the same proportion.

The addition of ammonia to the water in which the black powder is immersed, tends to prevent its spontaneous decomposition.

* Ann. Ch. Phys. [3] XV, 71.

Potash, on the contrary, accelerates it. So do acids in general. A solution of carbonate of potash has much the same action as pure water.

Chlorine destroys the black powder, but not instantaneously; bromine water causes its immediate decomposition. Strong nitric acid attacks it violently.

Hydrosulphuric acid causes its instant decomposition without the evolution of any gas, and with the formation of ammonia and hydriodic acid alone, sulphur being in the meantime deposited. This affords a ready method of determining the relative proportion of iodine and nitrogen. Accordingly, some of the black powder was diffused through water, and a stream of hydrosulphuric acid gas was passed through it, until the solution, which assumed at first a red tint, became colourless and smelt strongly of the gas. It was then gently heated and filtered; the hydriodic acid was precipitated as silver-salt, excess of silver was removed by the addition of a large excess of hydrochloric acid, and the resulting chloride of ammonium was estimated in the usual manner. The amount of ammonio-chloride of platinum obtained was 5·83 grs.; that of iodide of silver 12·53 grs., which is equivalent to

Nitrogen	0·366 grs.
Iodine	6·75 „

If we divide these numbers by the atomic weights of the respective elements, we obtain:

Nitrogen	261
Iodine.	533

or the proportion of 1 atom of nitrogen to 2·04 atoms of iodine.

The action of sulphurous acid appeared to offer the means of determining the relative proportion of nitrogen, iodine, and hydrogen also, if that element really be a constituent of the black powder. The transformation of the substance into ammonia and hydriodic acid takes place instantly, without the evolution of any gas, unless the temperature be suffered to rise considerably, when a secondary action is instituted. At the same time, a quantity of sulphurous acid is converted into sulphuric acid, equivalent of course to the quantity of water decomposed, in order to supply the necessary hydrogen. A carefully prepared fresh solution of sulphurous acid was added gradually to some of the black powder diffused through water, until the decomposition was complete. The solution thus obtained was divided into two equal portions. The one portion was evapo-

rated down with excess of hydrochloric acid, and the ammonia was converted into platinum-salt; the other portion was very gently warmed to expel sulphurous acid, nitrate of silver was added to precipitate the iodine, and subsequently the sulphuric acid was thrown down as baryta-salt. There were obtained 8·65 grs. of ammonia-chloride of platinum; 18·53 grs. of iodide of silver; and 17·57 grs. of sulphate of baryta. This is equivalent to

Nitrogen	0·542 grs.
Iodide	9·98 „
Sulphuric acid	6·04 „

Dividing these numbers by the atomic weights, we obtain:

Nitrogen	388	or 1	equiv.
Iodine	788	„ 2·03	„
Sulphuric acid . . .	1520	„ 3·92	„

This confirms the preceding result, and shows, moreover, that the black powder contains 1 equivalent of hydrogen; for 1 atom of ammonia, 2 atoms of iodine, and 4 atoms of sulphuric acid, can only arise from 4 atoms of sulphurous acid, 4 atoms of water, and NHI_2.

$$NHI_2 + 4\,SO_2 + 4\,HO = NH_3 + 2\,HI + 4\,SO_3.$$

Serullas* observed, that when this black powder is decomposed by dilute hydrochloric acid, a red solution is obtained, from which the addition of an alkali reprecipitates the explosive compound, a portion, however, being always decomposed into its elements. Millon† made the further observation, that if the black powder be treated with a saturated solution of hydrochloric acid, it disappears without the evolution of any gas, and the resulting solution is neutral to test paper. He believes that the substance is resolved into ammonia and the acids of iodine, and concludes from this peculiar reaction that the explosive body must have the composition $NH_2\,I$. It is difficult to see how this conclusion follows from the premises: the more natural idea would be, that the black powder, being ammonia in which a portion of the hydrogen is replaced by iodine, combines as such with the hydrochloric acid, thereby neutralising it. Yet Serullas has long since recorded various reasons tending to prove that this is not the case: he believed that the solution contained iodic and hydriodic acids, along with the hydrochloric acid; and what confirmed him in this belief, was the obser-

* Ann. Ch. Phys. XLII, 200. † Ann. Ch. Phys. [2] LXIX, 88.

vation, that when these two acids of iodine are mixed together, and supersaturated with ammonia, the explosive compound is obtained, especially if hydrochloric acid be present. Now, this certainly arises from the two acids, when mixed, reacting upon one another to produce free iodine; and the explanation of the eminent chemist just mentioned does not account for the fact, that, when the decomposition of the black powder has been effected by water, or other acids than the hydrochloric, a solution is obtained, from which ammonia does not reprecipitate it.

On repeating the experiment, I found that the red solution obtained by dissolving the explosive compound in strong hydrochloric acid, contains not a trace of free iodine; it gives no blue colour with starch. When evaporated to dryness in a water-bath, it comes out as a solid body of a somewhat yellow colour, soluble in water or alcohol, and neutral, or nearly so, to test paper. If potash or baryta-water be added to this solution, it re-precipitates the black powder. The addition of nitrate of silver causes a mixed precipitate of chloride and iodide of silver. Sulphurous acid gives rise to a separation of iodine, which a larger quantity converts into hydriodic acid. The dried substance, when heated *per se*, suffers decomposition; it gives off a pungent odour, then iodine sublimes, and afterwards chloride of ammonium. Ether extracts from the evaporated solution that which imparts to it its colour, and leaves some chloride of ammonium behind. All these reactions are perfectly explained by considering the solution produced by means of hydrochloric acid, as a mixture of chloride of ammonium and protochloride of iodine. The reaction is as follows:

$$NHI_2 + 3\,HCl = NH_4\,Cl + 2\,ICl.$$

And it has been already ascertained by Mitscherlich that the explosive compound is produced when protochloride of iodine is treated with ammonia. The reaction in this case will be:

$$2\,ICl + 3\,NH_3 = NHI_2 + 2\,NH_4\,Cl.$$

The same chemist states that terchloride of iodine with ammonia causes the formation of the same black powder. If this be really the case, we must suppose that some one of the oxygen-compounds of chlorine is formed at the same time. But an aqueous solution of terchloride of iodine is, to say the least, of very uncertain constitution; and even the liquid resulting from the action of *aqua regia* upon iodine may contain the protochloride. If iodic acid be dissolved by strong hydrochloric acid in the cold, a yellow solution

is obtained having a chlorous odour; but I find that the addition of ammonia causes no black precipitate in such a solution, unless it has been previously heated.

In accordance with the practice now adopted in naming those compounds, in which two equivalents of hydrogen in ammonia are replaced by two of another body, this explosive compound should bear the appellation "Iodimide."

When this paper was read before the Society, Dr. Playfair remarked, that some time since he had prepared the same explosive powder by pouring a solution of hypochlorite of lime into a solution of iodide of ammonium. He believed they were in the proportion of single equivalents; and as this reaction may be readily explained under the supposition that the compound is $NH_2 I$, it had confirmed in his mind the view propounded by Millon. Upon considering the reaction subsequently, I perceived that a compound, having Bineau's formula, might equally be obtained from the same salts in the same proportions, but that ammonia would appear among the products of decomposition. The reaction might be either

$$CaO, ClO + NH_4 I = NH_2 I + 2\,Ca\,Cl + 4\,HO$$

or

$$2(CaO, ClO) + 2\,NH_4 I = NH\,I_2 + 2\,Ca\,Cl + 4\,HO + NH_3$$

Upon repeating the experiment with bleaching powder, any alkaline reaction of which had been more than neutralized by acetic acid, I found a large quantity of ammonia set free. This reaction then, like every other with which I am acquainted, indicates the same composition for this explosive powder.

VII.—*Compound Testing Jet.*

By A. W. Hofmann, Ph.D., F.C.S.

The very extensive and daily increasing application of gas as a source of heat in chemical experiments, has suggested to me a small contrivance which is intended to facilitate the operations of the analyst.

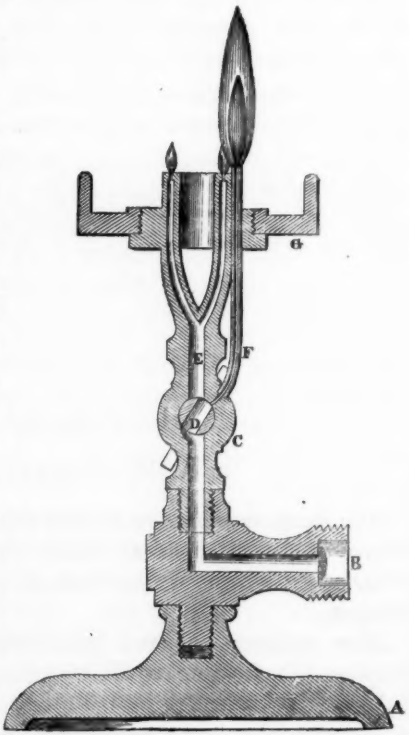
The ordinary Argand gas-burner which is almost universally employed for heating small vessels, such as flasks, retorts and test-tubes, is not adapted to the purposes of the blow-pipe. In operations with the latter instrument, a simple jet of gas is required,

issuing from a cylindrical orifice of rather considerable dimensions, the necessary amount of gas being adjusted by the stop-cock. This simplest of all gas-flames serves equally well for oxidation and reduction, and exhibits the phenomena of colour in the most conspicuous manner.

The ordinary method of analysis being a combination of testing in the moist way and by the blow-pipe, it is necessary either to use two gas-lamps—the one with the Argand burner, the other with the single jet—or to have a gas-stand so arranged as to admit of screwing on either the one or the other. But as it is inconvenient to multiply the number of gas-lamps, especially in a laboratory in which several analytical students are working, and as unscrewing hot gas-jets is a most unpleasant operation, I have endeavoured to unite the two jets in one stand, dispensing at the same time with the necessity of taking the apparatus to pieces.

The object in view is accomplished simply by substituting for the ordinary stop-cock a three-way cock.

The whole arrangement becomes at once intelligible by a glance at the wood-cut, which represents the burner half-size.



A is the loaded foot, into which the elbow-union-piece *B* is screwed. One end of this union is connected with a flexible pipe, not shown in the drawing; to the other screws the three-way stop-cock *C*. The plug *D* has only one orifice, and when turned in a vertical direction, supplies the Argand-burner through the perforation *E*. Into the side of the stop-cock is soldered a small pipe *F*, having a bore of about $\frac{1}{8}$ of an inch. This is prolonged to the distance of $\frac{1}{10}$ of an inch above the top of the Argand burner, where it is brazed to a small support for the blow-pipe, not represented in the drawing.

When the plug *D* is turned

in a horizontal direction, the gas is shut off from both jets, but when turned in an inclined position, may be made to supply both jets at once or either alternately. By this contrivance either of the jets will be lighted before the other is extinguished.

In order that the jet may be likewise used for heating larger apparatus, there is a support *G* on which may be fixed a copper chimney, either plain or provided with the wire-gauze for producing the air-flame.

The above burner has been made under the superintendence of Mr. J. J. Griffin, whose assistance I thankfully acknowledge.

VIII.—*On the Chemical Constitution and Nature of Organic Radicals.*

By H. Kolbe, Ph.D., F.C.S.

(*Conclusion.*)

Of all the chemical compounds with which we are as yet more intimately acquainted, no one is more nearly related to the alcohols, represented by the general formula $C_n H_{(n+2)} O_2$, than hydrated oxide of phenyl (phenylic acid) $(C_{12} H_5) O . HO$. If the general characters of the alcohols consist in their property of combining with sulphuric acid to form the so-called etherosulphuric acids; in the capability possessed by the oxides they contain, of simultaneously eliminating their water of hydration, and combining on the one hand with acids to form neutral salt-like compounds (the so-called compound ethers), and exchanging on the other hand, their oxygen for chlorine, bromine, sulphur, &c., whereby thus combinations similar to chloride or sulphide of ethyl are produced which may be re-converted into the corresponding alcohols; and, finally, if the alcohols are characterised by being converted, when heated with the hydrates of the alkalies or other oxidising agents, into the conjugate acids of their series,—oxide of phenyl may be said to fulfil these conditions, inasmuch as it combines with sulphuric acid to phenylosulphuric acid, $HO . SO_3 + (C_{12} H_5) O . SO_3$, which exchanges its basic atom of water for other bases, analogously to sulphovinic acid, thus yielding neutral double salts of oxide of phenyl with a metallic sulphate, which, on being heated, produce again hydrated oxide of phenyl. The analogy is carried out farther, by the

property of hydrate of phenyl, noticed by Laurent and Gerhardt* in their beautiful researches on the phenides, of combining, in the nascent state, with acids, for example with benzoic acid, to form a kind of ether corresponding to benzoic ether: $(C_{12}H_5)O.(C_{12}H_5)\urcorner C_2, O_3$ (benzoate of oxide of phenyl):

$(C_4 H_5)O.(C_{12}H_5)\urcorner C_2, O_2$ benzoate of oxide of ethyl,
$(C_{12}H_5)O.(C_{12}H_5)\urcorner C_2, O_3$ benzoate of oxide of phenyl,

which, by being heated with hydrate of potassa, is split again into its constituents, benzoic acid and hydrated oxide of phenyl. The latter substance participates likewise in the peculiarity of the alcohols, of yielding the haloïd-compounds of the radical corresponding to the oxides, if we may consider as such a compound the chloride of phenyl $(C_{12}H_5)Cl$, obtained by Gerhardt and Laurent† by the action of pentachloride of phosphorus upon hydrated oxide of phenyl, an ether-like substance, which is re-converted by boiling with solution of potassa into phenyloxide-potassa (phenylate of potassa).

With regard to the property of the alcohols, of being converted, by means of appropriate oxidising agents, into definite acids which contain the same amount of carbon, but two equivalents less of hydrogen, which are replaced by two equivalents of oxygen, the acid which corresponds to hydrated oxide of phenyl: $HO.(C_{10}H_3)\urcorner C_2, O_3$, is as yet unknown; it can however scarcely be doubted that we shall succeed in obtaining it directly from hydrated oxide of phenyl, as soon as proper energies have been directed towards filling up this gap.

Hydrated oxide of phenyl exhibits, on the other hand, very remarkable differences from the alcohols of the fatty acids. The oxides of the latter are mostly gifted with feebly basic properties, and combine with acids, particularly when they meet with them in the nascent state. The oxide of phenyl, however, which certainly forms similar combinations, although with much greater difficulty, is evidently possessed of a far greater tendency to perform the part of an acid. Like water and many metallic oxides which comport themselves with strong bases like acids, and with acids like bases, this substance is capable of entering into combination with both; forming apparently with the acids neutral compound ethers, but only when the acid itself is in the nascent state, as is, for instance, the case in the decomposition of the so-called chloride of benzoyl (dinoxy-chloride of benzoyl), by hydrated oxide of phenyl, into benzoate of oxide of phenyl. The hydrated oxide of phenyl combines, as is well known, with much

* Gerhardt et Laurent, C. R., 1849, 429.
† Gerhardt et Laurent, C. R., 1849, 435.

greater readiness with the alkalies directly, forming pure salts, from which it is separated unaltered by stronger acids, in the form of oily drops. Oxide of ethyl does not, however, appear to be totally devoid of acid properties. The two well-known crystallised salts, ethyl-oxide-potassa and ethyloxide-soda, are perfectly analogous to the phenyloxide-potassa.

A second, far more characteristic, difference between the phenyl-compounds and those of the common ether-radicals, consists in the proportionately much greater stability of phenyl, exhibited in an unequivocal manner by the remarkable metamorphoses which hydrated oxide of phenyl undergoes when acted upon by chlorine, bromine, or nitric acid. It can now be scarcely doubted any longer that chloro- bromo- and nitrophenylic acids still possess the original molecular grouping of phenylic acid, that they are true substitution-products, oxides of secondary phenyl-radicals, containing, in the place of two, three, or even more equivalents of hydrogen, an equal number of equivalents of chlorine, bromine, hyponitric acid, &c. We are already acquainted with the combinations of the following secondary radicals, derived from phenyl, of which it is as yet not determined whether they can also exist as such in the free state:

Phenyl = C_{12} H_5	Radical of Phenylic acid	
Chlorophenyl . .	$C_{12}\{H_4, Cl$	„ „ Chlorophenassic acid
Dichlorophenyl . .	$C_{12}\{H_3, Cl_2\}$	„ „ Chlorophenessic acid
Trichlorophenyl .	$C_{12}\{H_2, Cl_3$	„ „ Chlorophenissic acid
Pentachlorophenyl ?	C_{12} Cl_5 ?	„ „ Chlorophenussic acid
Tribromophenyl .	$C_{12}\{H_2, Br_3\}$	„ „ Bromophenissic acid
Dinitrophenyl . .	$C_{12}\{H_3, 2NO_4\}$	„ „ Nitrophenessic acid
Trinitrophenyl . .	$C_{12}\{H_2, 3NO_4\}$	„ „ Nitrophenissic acid (nitropicric acid)
Nitrodichlorophenyl	$C_{12}\{H_2, Cl_2, NO_4\}$	„ „ Nitrodichlorophenissic acid

A strong proof of the correctness of the view that trichlorophenylic, dinitrophenylic and trinitrophenylic acids are still possessed of the chemical constitution of phenylic acid and endowed with similar properties, appears to me to be furnished, on the one hand, by the fact, that the first of these, upon treatment with potassium-

amalgam, exchanges its chlorine gradually for hydrogen, and on the other hand, by the observation made by Gerhardt and Laurent, that the two nitrophenylic acids form, with benzoic acid, combinations quite similar to those of phenylic acid, compound ethers in which the dinitrophenylic and trinitrophenylic acids occupy the place of the base:

$(C_{12}\left\{\begin{matrix}H_3\\2NO_4\end{matrix}\right.)O \cdot (C_{12}H_5)\urcorner C_2, O_3$ benzoate of oxide of dinitrophenyl

$(C_{12}\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right.)O \cdot (C_{12}H_5)\urcorner C_2, O_3$ benzoate of oxide of trinitrophenyl.

Like the ether-radicals of the series $C_n H_{(n+1)}$, which are homologous to hydrogen, and which we must consider as produced by the combination of $C_n H_n$ with H, phenyl may also be considered as a repetition of hydrogen, namely, as hydrogen which has combined with the additional carbohydrogen $C_{12} H_4$. If this assumption is already justified by the analogy, just demonstrated, of the phenyl-alcohol with the hydrated oxides of the ether-radicals, it receives farther confirmation from the fact, that corresponding combinations of phenyl to the remaining manifold terms of the methyl-, ethyl-, amyl-series, &c., may be found with scarcely an exception. This analogy is most strikingly proved by the capability of phenyl of combining, like methyl, ethyl, &c., with 2 equivalents of carbon, to form a conjugate radical, the combinations of which exhibit the greatest similarity with those of acetyl, propionyl, &c. It is true, we have not yet succeeded in converting hydrated oxide of phenyl into the acid $HO \cdot (C_{12}H_5)\urcorner C_2, O_3$ in a similar manner to the conversion of hydrated oxide of methyl into acetylic acid, or, what is equivalent, in obtaining directly, from hydrated oxide of phenyl, the cyanide of phenyl, $(C_{12}H_5)$ Cy (benzonitrile), which yields benzoic acid by treatment with the alkalies or acids; but we must bear in mind that, as yet, only one method, of the many that may lead to this end, has been tried, namely, the distillation of phenylosulphate of baryta with cyanide of potassium (Hofmann).* A more favourable result might perhaps be obtained by an appropriate treatment of chloride of phenyl, discovered by Gerhardt and Laurent, with cyanide of potassium.

In making the well-founded assumption, that benzoic acid bears to hydrated oxide of phenyle the same relation as acetic acid to hydrated oxide of methyl, propionic acid to alcohol, and caproic acid

* Ann. Ch. Pharm. LXXIV, 32.

to hydrated oxide of amyl, it must be taken for granted, that all these acids are analogous in their constitution; and hence that benzoic acid likewise contains a conjugated radical, in which phenyl is the adjunct of C_2; benzoyl $= (C_{12}H_5)\frown C_2$. If we adopt this hypothesis, which likewise finds support in the arguments set forth in Vol. LXXV, p. 233, of Liebig's Annalen, the following formulæ will be the most simple expressions of the rational composition of the known benzoyl-compounds.

	Benzoyl $= (C_{12}H_5)\frown C_2$.		
Hydrated oxide of benzoyl	$HO.(C_{12}H_5)\frown C_2$,	O	Oil of bitter almonds.
Hydrosulphate of benzoyl.	$HS.(C_{12}H_5)\frown C_2$,	S	Sulphobenzole (Cahours*).
Hydrochlorate of chloride of benzoyl	$HCl.(C_{12}H_5)\frown C_2$,	Cl	Chlorobenzole (Cahours†).
Dinoxide of benzoyl	$(C_{12}H_5)\frown C_2$,	O_2?	Benzoeoxide (Berzelius‡).
Benzoylic acid	$HO.(C_{12}H_5)\frown C_2$,	O_3	Benzoic acid.
Dinoxichloride of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\Cl\end{matrix}\right.$	So-called Chlorobenzoyl.
Dinoxibromide of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\Br\end{matrix}\right.$	„ Bromobenzoyl.
Dinoxi-iodide of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\I\end{matrix}\right.$	„ Iodobenzoyl.
Dinoxicyanide of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\Cy\end{matrix}\right.$	„ Cyanobenzoyl.
Dinoxisulphide of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\S\end{matrix}\right.$	„ Sulphobenzoyl.
Dinoxamide of benzoyl	$(C_{12}H_5)\frown C_2$,	$\left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$	„ Benzamide.

SUBSTITUTION-PRODUCTS OF THE BENZOYL-COMPOUNDS.

Chlorobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.)\frown C_2$,	O_3	
Dichlorobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.)\frown C_2$,	O_3	
Trichlorobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right.)\frown C_2$,	O_3	
Bromobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_4\\Br\end{matrix}\right.)\frown C_2$,	O_3	
Nitrobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right.)\frown C_2$,	O_3	Nitrobenzoic acid.
Dioxamide of nitrobenzoyl	$(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right.)\frown C_2$,	$\left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$	
Dinitrobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_3\\2\,NO_4\end{matrix}\right.)\frown C_2$,	O_3	
Amidobenzoylic acid	$HO.(C_{12}\left\{\begin{matrix}H_4\\NH_2\end{matrix}\right.)\frown C_2$,	O_3	Benzimic acid. Benzamidic acid.

In whatever manner we view oil of bitter almonds, as the hydrogen-combination of the group $C_{12}H_5O_2$, as the second product

* Ann. Ch. Pharm. LXX, 41.

† Ann. Ch. Pharm. LXX, 40.

‡ Berzelius' Lehrbuch der Chemie, 5 Aufl., IV, 332.

of oxidation of the radical $C_{14}H_6$, or as the aldehyde of benzoic acid, its very numerous and complicated phenomena of decomposition, and particularly the metamorphoses which it undergoes with ammonia, present difficulties to each view which it is impossible at present to remove, but which will probably vanish upon a repetition of former researches, and a careful investigation of the various statements. At present, it appears to me that the manifold relations of oil of bitter almonds, particularly to the remaining benzoyl-combinations, may be best explained by the view upon which is founded the formula $HO.(C_{12}H_5)\urcorner C_2, O$; namely, that this substance is the hydrate of the lowest oxide of benzoyl, analogous to the aldehyde of acetic acid. Its behaviour with chlorine, in its conversion into dinoxichloride of benzoyl and hydrochloric acid:

$$HO.(C_{12}H_5)\urcorner C_2, O + 2\,Cl = (C_{12}H_5)\urcorner C_2, \left\{\begin{matrix} O_2 \\ Cl \end{matrix}\right. + H\,Cl.$$

certainly differs from that of aldehyde, inasmuch as the latter appears not to yield a dinoxichloride of acetyl, but to retain its basic atom of water unaltered, passing over, finally, into chlorale; this greater stability of the atom of water in aldehyde, may, however, be ascribed to the more powerfully acid properties of the latter, and its consequently greater affinity for the basic atom of water.

It must remain undecided, whether the compounds described by Cahours, the hydrosulphate of benzoyl and the hydrochlorate of chloride of benzoyl, possess a rational composition corresponding to the formulæ given above; their properties are still too little known to enable us to deduce therefrom reasons favourable to any one view. At any rate, the above view furnishes a perfectly satisfactory interpretation of the genetic relations of these two compounds to the hydrate of the oxide of benzoyl:

$$\underbrace{HO.(C_{12}H_5)\urcorner C_2, O}_{\text{Hydrate of oxide of benzoyl.}} + P\,Cl_5 = \underbrace{H\,Cl.(C_{12}H_5)\urcorner C_2, Cl}_{\text{Hydrochlorate of chloride of benzoyl.}} + P\left\{\begin{matrix} O_2 \\ Cl_3 \end{matrix}\right.$$

$$\underbrace{HCl.(C_{12}H_5)\urcorner C_2, Cl}_{\text{Hydrochlorate of chloride of benzoyl.}} + 2(KS.HS) = \underbrace{HS.(C_{12}H_5)\urcorner C_2, S}_{\text{Hydrosulphate of benzoyl.}} + 2KCl + 2HS$$

The hydrosulphobenzoyl, produced by the direct action of hydrosulphuric acid upon oil of bitter almonds, appears to be identical with the hydrosulphate of benzoyl.

The sulphobenzoic acid, discovered by Mitscherlich, which is formed under circumstances similar to those of nitrobenzoylic acid, classed above among the substitution-products of benzoylic acid (and which

must be viewed as the oxygen-compound of the secondary radical: $(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right)\urcorner C_2)$, is generally considered as analogous to the latter. The analogy of the mode of formation, and the rational composition of these two acids would be perfect, if the composition of the sulphobenzoic acid did correspond to the formula $HO\,.\,(C_{12}\left\{\begin{matrix}H_4\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3$, and saturated only 1 equiv. of base. It is, however, bibasic and contains, moreover, 1 equiv. more of sulphuric acid. I do not doubt, however, that sulphuric acid effects a perfectly similar metamorphosis of benzoylic acid to nitric acid, with this difference only, that the substitution-product corresponding to nitrobenzoylic acid, $HO\,.\,(C_{12}\left\{\begin{matrix}H_4\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3$, combines with an equivalent of sulphuric acid, forming a double acid, in which the two constituents, $(C_{12}\left\{\begin{matrix}H_4\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3$ and SO_3, retain their original saturating capacities. The composition of sulphobenzoic acid might therefore be expressed by the rational formula $2\,HO\,.\left\{\begin{matrix}(C_{12}\left\{\begin{matrix}H_4\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3,\\SO_3\end{matrix}\right.$ and its formation by the following equation:

$$\underbrace{HO\,.\,(C_{12}\,H_5)\urcorner C_2,\,O_3}_{\text{Benzoylic acid.}}+2\,SO_3=\underbrace{2\,HO\,.\left\{\begin{matrix}(C_{12}\left\{\begin{matrix}H_4\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3\\SO_3\end{matrix}\right.}_{\text{Sulphobenzoic acid.}}$$

Whether sulphurous acid be really capable of replacing 1 equiv. of hydrogen, as assumed in the above formula, cannot be decided *a priori*, but solely by facts. At any rate this assumption does not appear to be bolder than that of the displacement of hydrogen by hyponitric acid. Why should SO_2 not behave in a similar manner to NO_4?

In the formation of the so-called sulphacetic acid, we meet with a perfectly similar process of decomposition. Its rational formula: $2\,HO\,.\left\{\begin{matrix}(C_2\left\{\begin{matrix}H_2\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3,\\SO_3\end{matrix}\right.$ explains in a no less satisfactory manner its bibasic properties, and its relations to acetic acid:

$$\underbrace{HO\,.\,(C_2\,H_3)\urcorner C_2,\,O_3}_{\text{Acetic acid.}}+2\,SO_3=\underbrace{2\,HO\,.\left\{\begin{matrix}(C_2\left\{\begin{matrix}H_2\\SO_2\end{matrix}\right)\urcorner C_2,\,O_3\\SO_3\end{matrix}\right.}_{\text{Sulphacetic acid.}}$$

I do not consider it improbable that many of the organic acids, the chemical constitution of which is still unknown—such as malic acid, tartaric acid, &c.—will prove, on closer examination, to be conjugate acids, as suggested some time ago by Dumas and Piria,* and to which circumstance they will be found indebted for their polybasicity.

The above considerations lead to the question, whether the ether-radicals are not capable of combining with other elements, as they do with the adjunct C_2, to form similar conjugate radicals. I have no hesitation in answering this question affirmatively, and think that, before all, kakodyl must be viewed as a conjugate radical of this description, in which 2 equivs. of methyl form the adjunct of 1 equiv. of arsenic: kakodyl $= 2\,(C_2\,H_3)\urcorner As$. It has already been shown (in Vol. LXXV, p. 218 of Liebig's Annalen) how easily and naturally the formation of oxide of kakodyl is explained by this hypothesis. It may be applied without difficulty to all kakodyl-compounds, which have already been treated on this view in the "Handwörterbuch der Chemie," Vol. IV, p. 218 ff. I will not omit to mention here, that the highly interesting mode of formation of chloride of methyl, by heating kakodylate of superchloride of kakodyl, agrees with none of the views hitherto adopted of the constitution of the kakodyl-compounds, better than with the above assumption, that methyl is pre-existing in the radical.

The group of conjugate radicals discovered by Frankland, in which methyl, ethyl, &c., occur as adjuncts of the metals, zinc, tin, &c., is nearly related to kakodyl. In methyl-zinc, methyl-tin, ethyl-zinc, as in acetyl and kakodyl, the powers of affinity of the conjugate members: C_2, As, Zn, Sn, are not only considerably increased by their combination with the adjunct, but their boiling-points are also considerably diminished: these phenomena are probably in most intimate connection with each other, and may possibly arise from the assumption of a large amount of latent heat. A simple comparision of the boiling-points of the two corresponding acids, oxalic acid and acetylic acid, $HO\,.\,(C_2\,H_3)\urcorner C_2,\,O_3$, shows that the boiling temperature of the radical C_2 has decreased about 130°, by its combination with 1 equiv. of methyl, if a conclusion may be drawn, from the boiling-points of the combinations, as to those of the corresponding radicals C_2, and $(C_2\,H_3)\urcorner C_2$. In like manner the arsenic, combined with 2 equivs. of methyl (in kakodyl) is found to boil already at 170°, and methyl-zinc to be a very volatile liquid, spontaneously inflammable in the air.—Although attempts to prepare combinations of methyl-zinc and ethyl-zinc have as yet been unsuc-

* Ann. Ch. Pharm. XLIV, 70.

cessful, still it appears very probable that these bodies must be viewed as radicals, partly from their behaviour, and partly from observations, made by Frankland,* on the properties of the combinations of ethyl-tin (stannethyl), which are exceedingly similar to those of tin.

Conjugate radicals similar to those last mentioned, in which phenyl exists as the adjunct of metals, have not yet been obtained; the former appears, however, to exist, like the other ether-radicals, in conjugated combination with sulphur, and to form, with the latter, a radical corresponding to benzoyl: $(C_{12}\ H_5)\urcorner S_2$, which may be assumed as pre-existing in hyposulphobenzidic acid. Some years ago I described, in Liebig's Annalen, Vol. LIV, p. 145, four acids, very closely allied to each other, namely, chlorocarbohyposulphuric acid, chloroformylohyposulphuric acid, chlorelaylohyposulphuric acid, and methylohyposulphuric acid, of which the three latter may be produced directly from chlorocarbohyposulphuric acid, in a manner similar to the re-production of acetic acid from chloracetic acid. I have noticed, in the same memoir, the interesting relations existing, on the one hand, between chlorocarbohyposulphuric acid and chloracetic acid, and between methyloxalic acid and acetic acid, on the other hand, and have made the conjecture that they might, perhaps, possess an analogous chemical constitution. The less doubtful it appeared to me that chlorocarbohyposulphuric, and methylohyposulphuric acid (besides the intermediate acids), contain hyposulphuric acid in conjugate combination with various adjuncts, the greater was the support that I believed to have obtained for the view that the same adjuncts were contained in chloracetic and acetic acids, only in combination with oxalic acid in the place of hyposulphuric acid. As, however, these views have been modified since then, inasmuch as we no longer consider acetic acid as a conjugate oxalic acid, but as the oxygen-compound of the conjugate radical $(C_2\ H_3)\urcorner C_2$, it appears reasonable to entertain the opinion that those acids, considered hitherto as conjugate hyposulphuric acids, may be possessed of a rational composition corresponding to that of acetic acid. There is, in fact, nothing to prevent our assuming, in methylohyposulphuric acid, the existence of the conjugate radical $(C_2\ H_3)\urcorner S_2$, and to ascribe to the adjunct the capability of exchanging its hydrogen, like acetyl, for an equivalent quantity of chlorine, which would lead to the formation of the secondary radicals $(C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right)\urcorner S_2$, $(C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right)\urcorner S_2$, and $(C_2\ Cl_3)\urcorner S_2$, of which chloracetylo-, chloroformylo- and chloro-

* According to a private communication.

carbo-hyposulphuric acid must be considered as the oxygen compounds. As, according to Muspratt's experiments, the methylo-hyposulphuric acid, obtained by the oxidation of sulphocyanide of methyl by nitric acid, is identical with that obtained from chloro-carbohyposulphuric acid, the same view may also be extended to the homologous compounds formed by the oxidation of the sulpho-cyanides of ethyl and amyl, namely: ethylohyposulphuric acid, and amylohyposulphuric acid. The conjecture made just now, that hyposulphobenzidic acid might also possess a similar constitution, to which we may also add hyposulphotoluidic and hyposulphonaphthalic acids, does not appear to me to be met by any difficulties. Their mode of formation alone differs from that of methylo-, ethylo- and amylo-hyposulphuric acids; as the carbohydrogens of the series $C_n H_{(n+2)}$, corresponding to benzole, toluole, and naphthalole, namely: hydride of methyl (methylole, marsh-gas), hydride of ethyl (ethylole), and hydride of amyl (amylole), are known not to enter into any combination with fuming sulphuric acid. The latter appear, indeed, to possess in general a much greater stability than the former, as is shown particularly by the difference in their behaviour with fuming nitric acid; marsh-gas, at least, obtained by heating a mixture of acetate of soda and hydrate of lime, remains perfectly unaltered on treatment with nitric acid, even when passed through a mixture of the latter and concentrated sulphuric acid.

The following table of corresponding acids, the radicals of which consist, on the one hand of C_2, on the other of S_2, both combined with the same adjuncts, may serve for the farther elucidation of the foregoing:

Formylic acid.	Unknown.
$HO . H\frown C_2, O_3$	$HO . H\frown S_2, O_5$
Acetylic acid.	Methylodithionic acid.
$HO . (C_2 H_3)\frown C_2, O_3$	$HO . (C_2 H_3)\frown S_2, O_5$
Chloracetylic acid.	Chloromethylodithionic acid (chlorelaylohyposulphuric acid).
$HO . (C_2\{^{H_2}_{Cl}\})\frown C_2, O_3$	$HO . (C_2\{^{H_2}_{Cl}\})\frown S_2, O_5$
Dichloracetylic acid (unknown).	Dichloromethylodithionic acid (chloroformylohyposulphuric acid).
$HO . (C_2\{^{H}_{Cl_2}\})\frown C_2, O_3$	$HO . (C_2\{^{H}_{Cl_2}\})\frown S_2, O_5$
Trichloracetylic acid (chloracetic acid).	Trichloromethylodithionic acid (chlorocarbohyposulphuric acid).
$HO . (C_2 Cl_3)\frown C_2, O_3$	$HO . (C_2 Cl_3)\frown S_2, O_5$

Propionic acid.
$HO . (C_4 H_5)\widehat{}C_2, O_3$

Caproic acid.
$HO . (C_{10} H_{11})\widehat{}C_2, O_3$

Benzoic acid.
$HO . (C_{12} H_5)\widehat{}C_2, O_3$

Toluylic acid.
$HO . (C_{14} H_7)\widehat{}C_2, O_3$

Unknown.
$HO . (C_{20} H_7)\widehat{}C_2, O_3$

Ethylodithionic acid.
$HO . (C_4 H_5)\widehat{}S_2, O_5$

Amylodithionic acid.
$HO . (C_{10} H_{11})\widehat{}S_2, O_5$

Phenylodithionic acid
(hyposulphobenzidic acid).
$HO . (C_{12} H_5)\widehat{}S_2, O_5$

Kreotylodithionic acid*
(sulphobenzoic acid).
$HO . (C_{14} H_7)\widehat{}S_2, O_5$

Naphthylodithionic acid
(hyposulphonaphthalic acid).
$HO . (C_{20} H_7)\widehat{}S_2, O_5$.

The fact that acetyl and benzoyl combine in several proportions with oxygen, justifies the supposition that the radicals of methylodithionic acid $(C_2 H_3)\widehat{}S_2$, ethylodithionic acid $(C_4 H_5)\widehat{}S_2$, &c., might, perhaps, also combine with a smaller amount of oxygen. Sulphomethylosulphuric acid (Muspratt, "Annalen der Chemie," Vol. LXV, p. 261), the sulphethylosulphuric acid of Löwig and Weidmann, and the sulphamylosulphuric acid of Gerathewohl, might be looked upon as lower oxides of these radicals. The mode of formation of these acids, which are obtained by the oxidation of disulphide of methyl, hydrosulphate of sulphide of ethyl, and hydrosulphate of sulphide of amyl by nitric acid, differs so little from that of the above dithionic acids, with 5 equivs. of oxygen (which are obtained from the corresponding sulphocyanides), that one can scarcely imagine how different products can be formed under such equal circumstances. Add to this that their properties and those of their salts differ, according to the various statements, little or scarcely at all from those of the dithionic acids, and, finally, that nearly all the analytical results obtained with the so-called sulphomethylo-, sulphethylo- and sulphamylo-sulphates, correspond much better with the composition of the methylo-, &c., dithionates. The above reasons lead me to believe that the view, first entertained by Gerhardt, that Löwig's sulphethylosulphuric acid contains 5 equivs. of oxygen (in the anhy-

* The conjugate radicals of this second series of acids deserve particular names, as well as those of the first. I have called them dithionic acids, and have distinguished their adjuncts by placing their names in front. To the radical homologous to phenyl: $C_{14} H_7$, which is the adjunct in toluylic acid, I have given the name *kreotyl* (derived from kreosote), as I am of the opinion that kreosote is the homologous alcohol corresponding to hydrated oxide of phenyl; hydrated oxide of kreotyl, having the rational formula $(C_{14} H_7) O . HO$.

drous state) may be extended to the corresponding methyl- and amyl-compounds, although Muspratt (l. c.) has concluded, from his comparative investigation of sulphethylosulphuric acid and ethylodithionic acid, that they are different substances (comp. "Handwörterbuch der Chemie," Supplement, p. 73 ff. and 169 ff).—I will not omit to mention that the heavy, oily compound, the sulphethylosulphurous acid, discovered by Löwig and Weidmann, into which hydrosulphate of sulphide of ethyl is first converted by the action of nitric acid, and which is transformed, by continued treatment with nitric acid, into ethylodithionic acid, may be viewed, according to its composition, as a lower oxide of the radical $(C_4 H_5)\widehat{}S_2$, possessing the rational formula $(C_4 H_5)\widehat{}S_2, O_2$.

Although methyl, ethyl, amyl, phenyl, &c., are of themselves only repetitions of hydrogen (produced by the combination of additional carbohydrogens)* $C_2 H_2$, $C_4 H_4$, $C_{10} H_{10}$, and $C_{12} H_4$ with H, it is remarkable that they seem, notwithstanding, to possess the capability of combining with another equivalent of hydrogen to form binary compounds, hydrides, from which they may be made to pass over to other substances, as: chlorine, hyponitric acid, amidogen, &c. I have already, at an earlier period, made the conjecture† that marsh-gas did not possess the simple composition assigned to it by Berzelius, but that it might be the hydride of methyl $(C_2 H_3) H$; it appears to me that this view affords the best interpretation of its formation from acetates:

$$\underbrace{CaO \,.\, (C_2 H_3)\widehat{}C_2, O_3}_{\text{Acetate of lime.}} + CaO \,.\, HO = \underbrace{(C_2 H_3) H}_{\text{Hydride of methyl.}} + 2\,(CaO \,.\, CO_2)$$

This view has received a new support from the observation lately made by Frankland, that iodide of methyl and zinc, in the presence

* It would be desirable to follow a more definite rule and principle of nomenclature, in naming the different carbohydrogens, particularly those that occur frequently side by side, as $C_4 H_4$, $C_4 H_5$, and $C_4 H_6$. This might easily be effected by retaining the termination *yl* to the names of the radicals formed by the combination of homologous carbohydrogens with H, by giving to the homologous carbohydrogens and the analogues of $C_2 H_2$, $C_4 H_4$, &c., the names of the radicals, with addition of the terminating syllable *ene*, and by denoting the hydrides of the radicals by the terminating syllable *ole*, in the following manner:

$C_4 H_4$ Ethylene.	$C_{12} H_4$ Phenylene.	$C_{20} H_6$ Naphthalene.
$C_4 H_5$ Ethyl.	$C_{12} H_5$ Phenyl.	$C_{20} H_7$ Naphthyl.
$C_4 H_6$ Ethylole.	$C_{12} H_6$ Phenylole (benzole).	$C_{20} H_8$ Naphthalole (naphthalin).

† Handwörterbuch der Chemie, III, 700.

of water, or methyl-zinc and water, are decomposed into protoxide of zinc and hydride of methyl. Unfortunately, the chemical deportment of this hydride of methyl, as also that of the hydrides of ethyl and amyl, discovered by Frankland,* has been so little studied, that no arguments can be derived therefrom, either for or against the above view, unless I may perhaps mention here an observation made by Varrentrapp and myself, namely, that equal volumes of dry marsh-gas and chlorine yield, by exposure to diffused daylight, equal volumes of hydrochloric acid gas and a chlorinated inflammable gas, of which we have however as yet left undecided whether it is really chloride of methyl or an isomeric combination.

A much fitter means of testing this question is presented by the interesting metamorphoses of benzole, which stands in the same relation to benzoic acid and phenyl as hydride of methyl does to acetic acid and methyl. Its behaviour with nitric acid and sulphuric acid clearly shows that one equivalent of hydrogen exists in it in a different form to the remaining five. The question, how it is that benzole, in exchanging this one equivalent of hydrogen for NO_4 and passing over into nitrobenzole, changes its chemical character altogether, while, by the substitution of a second equivalent of hydrogen, a body is formed (dinitrobenzole) bearing the greatest similarity to nitrobenzole, may be easily answered, if we consider benzole as the hydrogen-compound of the phenyl-radical as hydride of phenyl $=(C_{12}H_5)H$, whereas the assumption, expressed by the old formula, $C_{12}H_6$, that all six equivalents of hydrogen are of equal value, renders no account whatever of the above circumstance. It is evident that, on the entrance of the first equivalent of hyponitric acid, in the place of the hydrogen that is combined with phenyl, there is formed nitrite of phenyl $=(C_{12}H_5)$, NO_4, the phenyl itself remaining unaltered. It is only by the action of a hot mixture of sulphuric and nitric acids, that the substitution of NO_4 for hydrogen is extended to the radical, the nitro-compound of the secondary radical: $C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right.$, namely, nitrite of nitrophenyl, $(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right.).NO_4$ (dinitrobenzole), being produced, which differs evidently not more from nitrite of phenyl than nitraniline does from aniline, methylodithionic acid from chloromethylodithionic acid, or nitrobenzoic acid from benzoic acid. Of all the reactions of dinitrobenzole, its behaviour with sulphide of ammonium shows most clearly that the two equivalents of NO_4 play a perfectly different part; for,

* Ann. Ch. Pharm. LXXI, 171; and LXXIV, 41.

on the conversion of dinitrobenzole into nitraniline, the equivalent of hyponitric acid, which occupies the place of hydrogen in the radical, remains unaltered; the conversion of NO_4 into amidogen is confined to the hyponitric acid existing in the compound externally of the radical atom:

$$\underbrace{(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right).NO_4}_{\text{Dinitrobenzole.}}+6HS=\underbrace{(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right).NH_2}_{\text{Nitraniline.}}+4HO+6S$$

The metamorphosis which benzole undergoes by treatment with sulphuric acid, namely, the formation of sulphobenzide and sulphobenzide-sulphuric acid, is also in perfect accordance with the above mode of viewing, if we consider sulphobenzide as phenylodithionic oxide $(C_{12}H_5).S_2,O_2$, and sulphobenzide-sulphuric acid as phenylodithionic acid $HO.(C_{12}H_5)\widehat{\ }S_2,O_5$ (corresponding to methylodithionic acid, &c.)

Attempts to prepare the chloride of the phenyl-radical from the hydride, by proper treatment with chlorine, have not hitherto been successful. The ultimate success of such experiments can however be doubted the less, since chloride of phenyl has been obtained in another way, by Laurent and Gerhardt, by the action of pentachloride of phosphorus on hydrated oxide of phenyl. Mitscherlich's chlorobenzide is perhaps a substitution-product of this substance, namely, the chloride of dichlorophenyl $(C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right)Cl$, and chlorobenzin is possibly a combination of the latter with 3 equivalents of hydrochloric acid: $C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right)Cl.3HCl$.

The homologues of benzole, namely: toluole, cumole and cymole, as also naphthalin, are so nearly allied to that substance, that I have no hesitation in ascribing to them a similar constitution and to consider them as composed according to the following rational formulæ: toluole $=(C_{14}H_7)H$; cumole $=(C_{18}H_{11})H$; cymole $=(C_{20}H_{13})H$; naphthalin $=(C_{20}H_7)H$. The radical $C_{20}H_7$ is the only one which we have not had as yet as adjunct of C_2 in a compound corresponding to acetic acid and benzoic acid; on the other hand, naphthylodithionic acid (hyposulphonaphthalic acid): $HO.(C_{20}H_7)\widehat{\ }S_2,O_5$, in which naphthyl is the adjunct of S_2, corresponds to methylodithionic acid and phenylodithionic acid (hyposulphobenzoic acid.)

The numerous derivatives of naphthalin, obtained therefrom by treatment with chlorine, bromine, nitric acid, &c., merit in a high degree the attention of chemists. There is perhaps no class of

bodies so well adapted to demonstrate in a convincing manner the insufficiency of the assumption of the immutability of organic radicals. All attempts to interpret the modes of formation of these derivatives of naphthalin, their metamorphoses and relations to each other, according to this view, may be considered as having totally failed. I shall therefore confine myself to giving an arrangement of those formulæ which I consider as the most probable expression of their rational composition; they are grounded upon the hypothesis, that naphthalin contains the radical $C_{20}H_7$ (naphthyl), and that the latter admits of the substitutions of its hydrogen by chlorine, hyponitric acid, &c, within a certain limit, without undergoing a farther change in the molecular grouping of its atoms.

Naphthyl = $C_{20}H_7$.		
Hydride of naphthyl	$(C_{20}H_7)H$	Naphtalin.
Chloride of naphthyl	$(C_{20}H_7)Cl$	Chlonaphthase.
Hydrochlorate of chloride of naphthyl	$(C_{20}H_7)Cl.HCl$	Souschlorure de naphtalaline, chloride of naphtalin, (Berzelius.)
Bromide of naphthyl	$(C_{20}H_7)Br$	Bronaphthase.
Hydrobromate of bromide of naphthyl	$(C_{20}H_7)Br.HBr$	Unknown.
Nitrite of naphthyl	$(C_{20}H_7)NO_4$	Nitronaphthalase.
Naphthylamine	$(C_{20}H_7)NH_2$	Naphthalidine.
Naphthylodithionic oxide	$(C_{20}H_7)SO_2$	Sulphonaphthalin, (Berz.)
Naphthylodithionic acid	$HO(C_{20}H_7)\frown S_2O_5$	Hyposulphonaphthalic acid, (Berz.)

SUBSTITUTION-PRODUCTS.

Chloride of chloronaphthyl	$(C_{20}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right.)Cl$	Chlonaphthese.
Dihydrochlorate of chloride of chloronaphthyl	$(C_{20}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right.)Cl.2HCl$	Chlorure de naphtaline, chloride of naphthaline, (Berzelius.)
Chloride of dichloronaphthyl	$(C_{20}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right.)Cl$	Chlonaphthise.
Dihydrochlorate of chloride of dichloronaphthyl	$(C_{20}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right.)Cl.2HCl$	Chlorure de chlonaphtase.
Chloride of trichloronaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right.)Cl$	Chlonaphtose.
Dihydrochlorate of chloride of trichloronaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right.)Cl.2HCl$	Chlorure de chlonaphtese.
Chloride of quintichloronaphthyl	$(C_{20}\left\{\begin{matrix}H_2\\Cl_5\end{matrix}\right.)Cl$	Chlonaphthalase.
Chloride of hypachloronaphthyl	$(C_{20}Cl_7)Cl$	Chlonaphthalise.

Bromide of bromonaphthyl	$(C_{20}\left\{\begin{matrix}H_6\\Br\end{matrix}\right.)Br$	Bronaphthese.
Bromide of dibromonaphthyl	$(C_{20}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right.)Br$	Bronaphthise.

Bromide of tribromonaphthyl . . .	$(C_{20}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right)Br$	Bronaphthose.
Hydrobromate of bromide of tribromonaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right)Br_2 . HBr$	Sousbromure de bronaphtise.
Dihydrobromate of bromide of tribromonaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right)Br . 2\,HBr$	Bromure de bronaphtese.
Dihydrobromate of bromide of quadribromonaphthyl	$(C_{20}\left\{\begin{matrix}H_3\\Br_4\end{matrix}\right)Br . 2\,HBr$	Bromure de bronaphtise.

Hydrochlorate of bromide of chloronaphthyl	$(C_{20}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right)Br . HCl$	Souschlorure de bronaphtase.
Chloride of chlorobromonaphthyl . .	$(C_{20}\left\{\begin{matrix}H_5\\Cl\\Br\end{matrix}\right)Cl$	Chlorebronaphtise.
Chloride of chlorodibromonaphthyl . .	$(C_{20}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right)Cl$	Chlorebronaphtose.
Dihydrobromate of chloride of chlorodibronaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right)Cl . 2\,HBr$	Bromure de chlonaphtese.
Chloride of dichlorobromonaphthyl . .	$(C_{20}\left\{\begin{matrix}H_4\\Cl_2\\Br\end{matrix}\right)Cl$	Chloribronaphthose.
Dihydrobromate of chloride of tribromomonaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right)Cl . 2\,HBr$	Bromure de chlorobronaphtese.
Dihydrochlorate of bromide of dichlorobromonaphthyl	$(C_{20}\left\{\begin{matrix}H_4\\Cl_2\\Br\end{matrix}\right)Br . 2\,HCl$	Chlorure de bronaphtese.
Bromide of trichlorobromonaphthyl . .	$(C_{20}\left\{\begin{matrix}H_3\\Cl_3\\Br\end{matrix}\right)Br$	Bromechlonaphtuse.
Dihydrochlorate of bromide of trichlorobromonaphthyl	$(C_{20}\left\{\begin{matrix}H_3\\Cl_3\\Br\end{matrix}\right)Br . 2\,HCl$	Chlorure de bromechlonaphtise.

Nitrite of nitronaphthyl	$(C_{20}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right) . NO_4$	Nitronaphthalese.
Nitrite of dinitronaphthyl . . .	$(C_{20}\left\{\begin{matrix}H_5\\2\,NO_4\end{matrix}\right) . NO_4$	Nitronaphthalise.
Chloride of dichlorodinitronaphthyl . .	$(C_{20}\left\{\begin{matrix}H_3\\Cl_2\\2\,NO_4\end{matrix}\right)Cl$	Binitronaphtaline bichloruré.

Chloronaphthylodithionic acid .	$HO . (C_{20}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique chloré.
Dichloronaphthylodithionic acid	$HO . (C_{20}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique bichloré.
Trichloronaphthylodithionic acid	$HO . (C_{20}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique trichloré.
Quadrichloronaphthylodithionic acid	$HO . (C_{20}\left\{\begin{matrix}H_3\\Cl_4\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique quadrichloré.

Bromonaphthylodithionic acid .	. HO . $(C_{20}\left\{\begin{matrix}H_6\\Br\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique bromé.
Dibromonaphthylodithionic acid	. HO . $(C_{20}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique bibromé.
Nitronaphthylodithionic acid .	. HO . $(C_{20}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right)\frown S_2, O_5$	Acide sulfonaphtalique nitré.

Thionaphthalic acid* . .	$2\,HO.\left\{\begin{matrix}(C_{20}\left\{\begin{matrix}H_6\\SO_2\end{matrix}\right)\frown S_2, O_5\\SO_3\end{matrix}\right.$	Acide thionaphtalique (Laurent.) Napthtinhyposulphuric acid, (Berzelius.)

The two highly remarkable compounds containing chlorine and oxygen, but no nitrogen, which Laurent has obtained by the action of nitric acid on the dihydrochlorate of chloride of dichloronaphthyl: $(C_{20}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right)\,Cl\,.\,2\,HCl$, and on chloride of quintichloronaphthyl $(C_{20}\left\{\begin{matrix}H_2\\Cl_5\end{matrix}\right)Cl$, possessing the empirical formulæ $C_{20}\,H_4\,Cl_2\,O_4$ and $C_{20}\,Cl_6\,O_4$, besides the acids obtained from the latter by treatment with potassa: $HO\,.\,C_{20}\,H_4\,Cl\,O_5$ (chloronaphthalic acid) and $HO\,.\,C_{20}\,Cl_5\,O_5$, appear to possess a rational composition corresponding to the salicyl- and anisyl-compounds (see further on) and to belong to the conjugate radicals $(C_{18}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}O_2)\frown C_2$ and $(C_{18}\,Cl_5\,O_2)\frown C_2$. Since Strecker† has called attention to the similarity existing between this chloronaphthalic acid and alizarin, both with respect to their composition (alizarin = $HO\,.\,C_{20}\,H_5\,O_5$) and properties, I scarcely consider it too bold an assumption to suppose that the primary radical of the above hypothetical radical $(C_{18}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}O_2)\frown C_2$, namely: $(C_{18}\,H_5\,O_2)\frown C_2$, exists in alizarin. I propose for it the name alizyl. The following rational formulæ appear to me to afford the best interpretation of the mutual relations of the above compounds:

	Alizyl = $(C_{18}\ H_5\ O_2)\frown C_2$	
Dinoxychloride of alizyl . .	. $(C_{18}\ H_5\ O_2)\frown C_2, \left\{\begin{matrix}O_2\\Cl\end{matrix}\right.$	Unknown.
Alizylic acid . .	HO . $(C_{18}\ H_5\ O_2)\frown C_2, O_3$	Alizarin.
Dinoxychloride of chloralizyl	. $(C_{18}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}O_2)\frown C_2, \left\{\begin{matrix}O_2\\Cl\end{matrix}\right.$	Oxide de chloroxénaphtose, (Laurent.)

* Conjugate acid of thionaphthylodithionic acid and sulphuric acid.

† Handwörterbuch der Chemie von Liebig, Poggendorff and Wöhler, IV, 598. Art. Madder.

Chloralizylic acid	$HO . (C_{18}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}O_2)\urcorner C_2, O_3$	Chloronaphthalic acid.
Dinoxychloride of pentachloralizyl.	$(C_{18} Cl_5 O_2)\urcorner C_2, \left\{\begin{matrix}O_2\\Cl\end{matrix}\right.$	Oxide de chloroxénaphtalise. (Laurent.)
Pentachloralizylic acid.	$HO . (C_{18} Cl_5 O_2)\urcorner C_2, O_3$	Acide chloroxénaphtalésique. (Laurent.)

Hofmann, in his latest excellent researches on the volatile bases,* has already expressed the opinion, that there are probably two corresponding series of organic bases, amidogen- and ammonia-bases, and that the existence of amidogen-bases, in which we assume, with Liebig, amidogen in combination with a compound radical, does not necessarily preclude the existence of ammonia-bases, in which we imagine ammonia as pre-existing in combination with a compound body. While thiosinamine, thialdine, the ureas, and many vegetal bases, the chemical constitution of which is as yet perfectly unknown, may perhaps belong to the latter series, Hofmann is certainly right in viewing the volatile bases described by himself and Wurtz, as the amidogen-combinations of compound radicals, as analogues of ammonia of which the one (radical-) equivalent of hydrogen is replaced by a compound radical:

Ammonia . .	$H . NH_2$	
Methylamine . .	$(C_4 H_5) . NH_2$	
Phenylamine . .	$(C_{12} H_5) . NH_2$	(Aniline).
&c.	&c.	

Another argument might be added to the many proofs already established by Hofmann, in favour of the view, that ethylamine, aniline, &c., are really amidogen-combinations of the radicals $C_4 H_5$ and $C_{12} H_5$, and have not, according to Berzelius' mode of viewing, to be considered as conjugate ammonias (with the adjuncts $C_4 H_4$ and $C_{12} H_4$). The important discovery, that bromide of ethyl and ammonia are transformed into hydrobromic acid and ethylamine:

$$\underbrace{(C_4 H_5) Br}_{\text{Bromide of ethyl.}} + \underbrace{H . NH_2}_{\text{Ammonia.}} = \underbrace{(C_4 H_5) . NH_2, H Br}_{\text{Hydrobromate of ethylamine.}} .$$

and that nitrous acid reconverts ethylamine into an oxygen- compound of ethyl, namely, into nitrite of oxide of ethyl, appears to me to place the question of the chemical constitution of ethylamine parallel with the question whether we should consider bromide of ethyl as the bromide of the ethyl-radical, or as hydrobromic acid

* Ann. Ch. Pharm. LXXIV, 125.

combined with $C_4 H_4$, viz., as $C_4 H_4 . H Br$. It would, according to the above facts, be perfectly inconsistent to view ethylamine as ammonia conjugated with $C_4 H_4$, and as expressed by the rational formula $(C_4 H_4) . NH_3$, or $(C_4 H_4), (H . NH_2)$; bromide of ethyl, on the other hand, being assumed as the ethyl-radical combined with bromine.

An objection that has been repeatedly raised against the view, that organic nitrogenised bases are amidogen-compounds, is, that amidogen has not the property of forming bases, in support of which have been quoted amide of potassium, oxamide, oxamic acid, &c., of which it cannot be doubted that they contain amidogen, none of which are however endowed with basic properties. This kind of argument might certainly be classed with the no less paradoxical assertion that hydrochloric acid contains no chlorine, because the latter forms neutral or indifferent bodies with potassium, carbon, &c. The difference between chloride of potassium, chlorobenzoyl $(C_{12} H_5)^{\frown}C_2, \left\{\begin{matrix} Cl \\ C_2 \end{matrix}\right.$ and hydrochloric acid is not less than that between amide of potassium, benzamide $(C_{12} H_5)^{\frown}C_2, \left\{\begin{matrix} O_2 \\ NH_2 \end{matrix}\right.$ and ammonia.

It cannot be doubted, that the chemical nature of the amidogen-compounds, exactly as with the chlorine-compounds, is essentially modified, as well by the nature of the body with which amidogen combines, as by the part which it has to play in such combinations. While, in amide of potassium, it appears to play the part of a salt-former, it is found in oxamide $C_2, \left\{\begin{matrix} O_2 \\ NH_2 \end{matrix}\right.$, benzamide, acetamide, &c., to occupy the place of oxygen. From all these compounds, to which may be added the amidogen-acids, it may be expelled with facility, as ammonia, and oxygen may enter into its place. In amidobenzoylic acid: $HO . C_{12} \left\{\begin{matrix} H_4 \\ NH_2 \end{matrix}\right.)^{\frown}C_2, O_3$ (benzimic acid), the amidogen appears to occupy the place of hydrogen, as the chlorine does in chlorobenzoylic acid: $HO . (C_{12} \left\{\begin{matrix} H_4) \\ Cl \end{matrix}\right.)^{\frown}C_2, O_3$, and it cannot be detected in this compound by the ordinary means, any more than the chlorine can in the last-named acid. It is well known, that on boiling these substances with solution of potassa, neither ammonia is given off on the one hand, nor chloride of potassium formed on the other. Can it appear strange, after these statements, that amidogen should combine and form bases with hydrogen and its analogues, methyl, phenyl, &c.; that it exercises the functions of a base-former in organic

bases? The analogy of the different functions, which amidogen and chlorine exercise, would be perfect if the chlorides of methyl and ethyl, in fact, all the chlorine-compounds of the homologues and analogues of hydrogen were equally similar in their properties to hydrochloric acid, as methylamine, ethylamine, phenylamine, &c., are to ammonia.

Methylamine and ammonia, which, according to Wurtz, correspond so closely in their chemical behaviour, and even in their physical properties, that their compounds can only be distinguished from each other by analysis, may be compared in this respect to acetic and formic acids, which contain the same radicals as adjuncts, and do likewise not differ much more in their properties than those two bases:

Formic acid .	$HO.\ H\urcorner C_2,\ O_3$	$H\ .\ NH_2$	Ammonia.
Acetic acid .	$HO.(C_2H_3)\urcorner C_2,\ O_3$	$(C_2H_3).NH_2$	Methylamine.
Propionic acid.	$HO.(C_4H_5)\urcorner C_2,\ O_3$	$(C_4H_5).NH_2$	Ethylamine.
Caproic acid .	$HO.(C_{10}H_{11})\urcorner C_2,\ O_3$	$(C_{10}H_{11}).NH_2$	Amylamine.
Benzoic acid .	$HO.(C_{12}H_5)\urcorner C_2,\ O_3$	$(C_{12}H_5).NH_2$	Aniline.
Toluylic acid .	$HO.(C_{14}H_7)\urcorner C_2,\ O_3$	$(C_{14}H_7).NH_2$	Toluidine.
	&c.	&c.	

On a closer examination and comparison of the above compounds, it will be seen, that what has been said (in Liebig's Annalen, pp. 225 and 233) of the comparatively subordinate influence exercised by the adjuncts of the above acids over the chemical character of the latter, may be almost equally applied to the amines of the same carbohydrogens. For, with whatever carbohydrogen (radical) the amidogen may be combined,—provided that it is an analogue of hydrogen,—the resulting amines possess the peculiar chemical character of their prototype ammonia to such a degree, that they would be always regarded as imitations of ammonia, even if their rational composition were unknown. In the same manner as the member C_2, occurring in the above acids in combination with different adjuncts, gives the principal stamp to the character of the resulting conjugate radicals, formyl, acetyl, &c., and their combinations, the corresponding amines appear to owe their basic nature almost exclusively to amidogen.

Hofmann's important discovery, that several equivalents of hydrogen in the radical of aniline, may even be replaced by chlorine, iodine, hyponitric acid, &c., and that their products of substitution, chloraniline: $(C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right).NH_2$, dichloraniline: $(C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right).NH_2$, nitra-

niline : $(C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right).NH_2$, &c., are still possessed of basic properties, proves most indisputably how little in general the basicity of the amines is dependent upon the nature and composition of their radicals. These facts appear, at a cursory glimpse, to be favourable to the hypothesis constructed by the adherents to the theory of types, that the part which an element plays in organic composition is not dependent upon its original properties, but solely upon the position which it occupies in the combination. Upon closer investigation of the question, it will however be found, that Hofmann's investigation of the chlorinated bases contains indeed the refutation of those extreme views. That chemist has shown, that the basicity of aniline decreases in an inverse proportion to the number of the equivalents of chlorine and bromine introduced in the place of hydrogen. Bromaniline is still a tolerably powerful base, though weaker than aniline itself, dibromaniline likewise still possesses basic properties, its salts exhibit however but very slight stability; tribromaniline, finally, is no longer basic, but is, like trichloraniline, a perfectly indifferent body. Bromine has therefore evidently imparted a portion of its original (negative) character to the compound, into which it has entered in the place of hydrogen; the fundamental properties of aniline, among which its basic nature must unquestionably be reckoned as of the highest importance, are more or less modified, in consequence of the above process of substitution; they are therefore not exclusively conditional upon the equality of the position of the elements.

Hofmann's latest, and highly important discovery, that all three equivalents of hydrogen in ammonia may be successively replaced by the so-called ether-radicals, without the original basic character of the ammonia being lost, is not only of the greatest interest to the radical theory, inasmuch as it appears to me to place beyond all doubt the existence of compound radicals, but promises also to throw, quite unexpectedly, new light upon the chemical constitution of many organic bases, hitherto not properly understood. The remarkable isomerism of toluidine: $(C_{14}H_7).NH_2$, and methylaniline: $(C_{12}H_5).N\left\{\begin{matrix}C_2H_3\\H\end{matrix}\right\}$, would, if we were unacquainted with the mode of formation of the latter, be to us equally enigmatical to the hitherto inexplicable isomerism of aniline and picoline.—As we have well-founded reasons for viewing aniline as composed according to the rational formula $(C_{12}H_5).NH_2$, we may imagine picoline to be a methylated base, analogous to methylamine, perhaps

$$(C_{10}\,H_3)\,.\,N\left\{\begin{matrix}C_2\,H_3\\H\end{matrix}\right\}\text{ or }(C_2\,H_3)\,.\,N\left\{\begin{matrix}C_{10}\,H_3\\H\end{matrix}\right\}.$$

If this assumption be well founded, picoline would, according to the experience we possess up to the present time, only admit of the entrance of *one* atom of an ether-radical in place of its hydrogen; this might be easily decided by a simple experiment.

Since the one (radical-) equivalent of hydrogen in ammonia is possessed of functions different from those of the two others in amidogen, the question arises which of the three equivalents of hydrogen is first replaced by ethyl, in the conversion of ammonia into ethylamine (by treatment of the former with bromide of ethyl); or in other words, whether the rational formula $(C_4\,H_5)\,.\,NH_2$, or $H\,.\,N\left\{\begin{matrix}C_4\,H_5\\H\end{matrix}\right\}$ must be assigned to ethylamine. The facility with which amidogen may be transferred from the radical-hydrogen to other combinations, for instance, in the formation of oxamide, benzamide, &c., evidently imparts the greatest degree of probability to the first formula, which is also generally adopted. The formation of aniline from nitrobenzole can scarcely be made to accord with any other formula for aniline than $(C_{12}\,H_5)\,.\,NH_2$. If, therefore, we should succeed at some future period in producing this base in the same manner as ethylamine—perhaps by the action of ammonia on the hitherto unknown bromide of phenyl, $(C_{12}\,H_5)\,Br$,—which cannot be regarded as unlikely, or in producing from hydride of ethyl a nitrite of ethyl: $(C_4\,H_5)\,.\,NO_4$, and from this, ethylamine,—the correctness of the view, that the first substitution of the one equivalent of hydrogen in ammonia occurs with the radical-hydrogen, might be considered as pretty well proved.

The extent to which methyl, ethyl, and the so-called ether-radicals in general are capable of playing the part of hydrogen in organic combinations, is most clearly shown by the remarkable combination of iodide of ethyl with triethylamine discovered by Hofmann, the hydriodate of ammonia in which all the equivalents of hydrogen are replaced by ethyl, $(C_4\,H_5)\,.\,N\,2(C_4\,H_5)$, $(C_4\,H_5)\,I$, as also by the oxygen-base obtained therefrom, $(C_4\,H_5)\,.\,N\,2(C_4\,H_5)$, $(C_4\,H_5)\,O\,.\,HO$, which represents, in the ethyl-series, the member that is wanting in the ammonia-series: hydrated oxide of ammonium. There can, I think, exist no more simple or decided proof of the existence of compound radicals, than these methylated or ethylated bases.

It is a circumstance worthy of notice, that methylaniline, although it contains the elements of $C_2\,H_2$ more than aniline, has a boiling-

point only 10° C. higher than the latter (192°), while the isomeric toluidine boils at 200°. Again, ethylaniline only boils 22° higher than aniline, notwithstanding the difference existing between them of 2 ($C_2 H_2$). Diamylaniline, which contains 10 ($C_2 H_2$) more than aniline, and should therefore have a boiling-point about 200° higher than the latter, boils at a temperature only 100° higher than aniline; lastly, the boiling-point of amylethylaniline (262°), which contains 7 ($C_2 H_2$) more than aniline, exceeds that of the latter only by 80°, instead of 140°, which is therefore, likewise, only half the ordinary increase.

It hence appears, as though the entrance of $(C_2 H_2)_n$ into organic combinations, effects, at times, only half the increase in the boiling-point that one is accustomed to expect, and as though the form in which the homologising carbohydrogen is added to the compound, had no unimportant influence over this point. The above observations are at least in favour of the view, that where this carbohydrogen, in the form of methyl, ethyl, &c., replaces the hydrogen exterior of the radical, the boiling-point of the combination rises only one half the amount that it does in cases where the carbohydrogen enters into the place of the radical itself. At any rate, it appears to me to show, in a most decided manner, that the regularity of the increase in boiling-points, caused by the entrance of certain elements into organic combinations, is subject to many encroachments.

The conversion of organic amines, by the removal of 1 equivalent of hydrogen, into compound amides, which bear the same relation to the former as the simple amides to ammonia, can be explained in a simple manner, only by the assumption that this elimination of hydrogen takes place in the radical combined with the amidogen, the amidogen itself remaining unaltered; that, therefore, there is formed from aniline $(C_{12} H_5) . NH_2$, anilide of the rational composition $(C_{12} H_4)\overset{\frown}{}NH_2$; from naphthalidine $(C_{20} H_7) . NH_2$, a naphthalidide = $(C_{20} H_6)\overset{\frown}{}NH_2$; from nitraniline $(C_{12} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right.) . NH_2$, a nitranilide = $(C_{12} \left\{ \begin{matrix} H_3 \\ NO_4 \end{matrix} \right.)\overset{\frown}{}NH_2$. The question now at once arises, how it can be explained that bodies of so similar a composition as aniline and anilide possess such different properties; that amidogen, in combination with the one carbohydrogen $C_{12} H_5$ should form a base, while it forms with the other, $C_{12} H_4$, a body bearing a much greater resemblance to chlorine and oxygen? This question may be easily answered, if the fact be borne in mind that, besides hydrogen itself,

only those compound radicals that are homologous or analogous to it are capable of producing bases with amidogen, or, in general, only radicals that can play the part of hydrogen, as ethyl, phenyl, naphthyl, &c., among which must also necessarily be included the secondary radicals derived from them, for instance, chlorophenyl: $C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}$, nitrophenyl: $C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}$, &c. The so-called additional carbohydrogens: C_2H_2, C_4H_4, $C_{12}H_4$, $C_{20}H_6$, &c., by the combination of which with 1 equivalent of hydrogen we imagine the above radicals produced, and which evidently fulfil functions quite different from the latter, must not be confounded or placed in the same rank with them. Incapable themselves of playing the part of hydrogen, or indeed of a radical, and therefore incapable of forming bases in combination with amidogen, but apparently only destined to produce series of analogous combinations, these carbohydrogens only give rise, by combination with amidogen, to a series of different amides, which still possess to a full extent, the general characters of the simple amides. Anilide $(C_{12}H_4)\smile NH_2$ is a true amide, the properties of which are not altered to a greater extent by the addition of $C_{12}H_4$, than those of formic acid $HO.H\frown C_2,O_3$, in its conversion into benzoic acid $= HO.(C_{12}H_5)\frown C_2,O_3$, by the assumption of the same additional carbohydrogen in the adjunct of its radical.

The following very simple expressions are obtained for the rational composition of the corresponding amides and anilides, amidic and anilidic acids, by representing anilide $(C_{12}H_4)\frown NH_2$ by And, in the same manner as amidogen is represented by Ad.

AMIDES.		ANILIDES.	
Carbamide	$C\left\{\begin{matrix}O\\Ad\end{matrix}\right.$	Carbanilide	$C\left\{\begin{matrix}O\\And\end{matrix}\right.$
Oxamide	$C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.$	Oxanilide	$C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.$
Benzamide	$(C_{12}H_5)\frown C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.$	Benzanilide	$(C_{12}H_5)\frown C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.$
Cumamide	$(C_{18}H_{11})\frown C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.$	Cumanilide	$(C_{18}H_{11})\frown C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.$
Succinamide	$(C_2H_2)\smile C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.$	Succinanilide	$(C_2H_2)\smile C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.$
Suberamide	$(C_6H_6)\smile C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.$	Suberanilide	$(C_6H_6)\smile C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.$
&c.		&c.	

AMIDIC ACIDS.

Sulphamic acid . . $HO.S\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.; SO_3$

Carbamic acid . . $HO.C\left\{\begin{matrix}O\\Ad\end{matrix}\right.; CO_2$

Oxamic acid . . $HO.C_2\left\{\begin{matrix}O_2\\Ad\end{matrix}\right.; C_2O_3$

&c.

ANILIC ACIDS.

Sulphanilic acid . $HO.S\left\{\begin{matrix}O_2\\And\end{matrix}\right.; SO_3$

Carbanilic acid . . $HO.C\left\{\begin{matrix}O_2\\And\end{matrix}\right.; CO_2$

Oxanilic acid . . $HO.C_2\left\{\begin{matrix}O_2\\And\end{matrix}\right.; C_2O_3$

&c.

It is a remarkable, and certainly not purely accidental circumstance, that a portion only of the acids that yield amides form also amidic acids and imides. With the exception of benzimide, of which it is more than doubtful whether it may be reckoned among the imides, there exist neither amidic acids nor imides of the fatty acids, and those nearly related to them, such as benzoic acid, toluylic acid, &c. On examining the series of known amidic and anilidic acids, imides and aniles, it will be observed that these compounds are formed exclusively from those acids which are capable of existing in the anhydrous state, and are at the same time particularly inclined to form acid salts, such as sulphuric acid, carbonic acid, oxalic acid, besides the whole series of acids so nearly related to the latter: succinic acid, suberic acid, camphoric acid, phtalic acid, &c. It must remain undecided whether the peculiarity of these acids of being capable of existing even without their basic atom of water, is necessarily in some connection with their capability of forming amidic acids and imides; we may perhaps expect some further elucidation of this subject as soon as we are better acquainted with the nature of these combinations, particularly of the imides.

With regard to the chemical constitution of the imides, which we do not yet understand, the interesting observations made by Dumas, Malaguti, and Leblanc, that the amides are converted into cyanogen-compounds by the abstraction of water—acetamide,

$(C_2 H_3)\frown C_2, \left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$ into the cyanide*) of its adjunct, cyanide of methyl, $(C_2 H_3)\frown C_2 N$; benzamide, $(C_{12} H_5)\frown C_2, \left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$ into cyanide of phenyl: $(C_{12} H_5)\frown C_2 N$ (benzonitrile)—appears to afford a new point of view from which to investigate this question. I consider it as not improbable, that in the conversion of amidic acids into imides by the elimination of 2 equivalents of water, the process by which it is effected is the same as in the formation of cyanide of methyl from acetamide, or in other words, that the imides consist of 1 equivalent of the hydrated acid, combined with a cyanogen-compound. If we express the rational composition of an amidic acid, of which there also exists an amide, by the general formula: $HO . P\smile C_2, \left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$; $P\smile C_2, O_3$ (in which P represents the adjunct of the acid), the formula $HO . P\smile C_2 N$; $P\smile C_2, O_3$ would be the rational expression of the composition of the corresponding imide, and the conversion would proceed according to the following equation:

$$\underbrace{HO.P\smile C_2\left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.; P\smile C_2, O_3}_{\text{Amidic acid.}} = \underbrace{HO . P\smile C_2 N; P\smile C_2 O_3}_{\text{Imide.}} . + 2\ HO.$$

This hypothesis, by which the acid properties of the imides are likewise accounted for, requires that we should assume in the acids yielding imides, namely, succinic acid, suberic acid, phtalic acid, camphoric acid, &c., 2 equivalents of carbon, combined with an adjunct, as in the fatty acids. These adjuncts differ, however, mainly from those in the fatty acids, in not consisting of ether-radicals, but of the homologising carbohydrogens themselves: $C_2 H_2$, $C_4 H_4$, &c. In the same manner, therefore, as acetic acid, butyric acid, &c., may be viewed as repetitions of formic acid, the former may be considered as repetitions of oxalic acid:

Oxalic acid .	$HO. \quad C_2, O_3$	$HO. \quad H\frown C_2, O_3$	Formic acid.
Succinic acid	$HO.(C_2 H_2)\smile C_2, O_3$	$HO.(C_2 H_3)\frown C_2, O_3$	Acetic acid.
Adipinic acid	$HO.(C_4 H_4)\smile C_2, O_3$	$HO.(C_4 H_5)\frown C_2, O_3$	Propionic acid.
Suberic acid.	$HO.(C_6 H_6)\smile C_2, O_3$	$HO.(C_6 H_7)\frown C_2, O_3$	Butyric acid.
	&c.	&c.	

* There might possibly exist two isomeric combinations of the empirical composition: $C_4 H_3 N$, one of which might be the nitrogen-combination of the conjugate radical $(C_2 H_3)\frown C_2$, namely $(C_2 H_3)\frown C_2, N$ (cyanogen, the carbon of which has the adjunct, methyl); the other, the real cyanide of methyl: $(C_2 H_3)\frown C_2 N = (C_2 H_3)$, Cy. In like manner benzonitrile might perhaps be viewed as $(C_{12} H_5)\frown C_2 N$, differing from the still unknown, true cyanide of phenyl $(C_{12} H_5)$, Cy.

Many chemists, who consider the acids analogous to oxalic acid, as also the combinations belonging to this series: camphoric acid, phtalic acid, pyrotartaric acid, &c., as bibasic acids, double their atomic weight. If this view, which is supported by a number of facts, should be correct, the kind of composition with which we have already become acquainted, in speaking of sulphobenzoic and sulphacetic acids, may perhaps furnish us with a key to the proper understanding of the chemical constitution of those conjugate oxalic acids. These may be viewed in a similar manner to the above-mentioned, as compound acids of oxalic acid and another conjugate oxalic acid, in the following manner:

Oxalic acid . . . . . $HO . C_2 O_3$

Succinic acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_4 & H_4 \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Pyrotartaric acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_6 & H_6 \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Adipic acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_8 & H_8 \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Pimelic acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_{10} & H_{10} \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Suberic acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_{12} & H_{12} \\ C_2 & O_3 \end{matrix} \right) \frown O_3$

Phtalic acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_{12} & H_4 \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Camphoric acid . . . . . $2\,HO . \left\{ \begin{matrix} (C_{16} & H_{14} \\ C_2 & O_3 \end{matrix} \right) \frown C_2 O_3$

Hyposulphosuccinic acid . . . $3\,HO . \left\{ \begin{matrix} (C_4 \left\{ \begin{matrix} H_3 \\ SO_2 \end{matrix} \right) \frown C_2 O_3 \\ C_2 \quad O_3 \\ S \quad O_3 \end{matrix} \right.$

According to the above view, the composition of their amidic acids and imides would be expressed by the following rational formulæ:

Succinamic acid . . $HO . (C_4 H_4) \frown C_2 \left\{ \begin{matrix} O_2 \\ NH_2 \end{matrix} \right\} ; C_2 O_3$

Phtalamic acid . . . $HO . (C_{12} H_4) \frown C_2 \left\{ \begin{matrix} O_2 \\ NH_2 \end{matrix} \right\} ; C_2 O_3$

Camphoramic acid . . $HO . (C_{16} H_{14}) \frown C_2 \left\{ \begin{matrix} O_2 \\ NH_2 \end{matrix} \right\} ; C_2 O_3$

&c.

Succinimide . . $HO . (C_4 H_4) \frown C_2 N ; C_2 O_3$

Phtalimide . . . $HO . (C_{12} H_4) \frown C_2 N ; C_2 O_3$

Camphorimide . . $HO . (C_{16} H_{14}) \frown C_2 N ; C_2 O_3$

&c.

I do not deny that difficulties are met with in following up this hypothesis still farther. Among others, it would be necessary to assume, in the aniles, for instance, in succinanile, the existence of the very hypothetical compound $N\breve{}(C_{12}H_4)$, combined with $(C_4H_4)\breve{}C_2$ and forming a peculiar cyanogen, in which the carbon as well as the nitrogen are each joined with an additional carbohydrogen; thus succinanile would be $= HO.(C_4H_4)\breve{}C_2\ N\breve{}(C_{12}H_4),\ C_2O_3$; phtalanile $= HO.(C_{12}H_4)\breve{}C_2\ N\breve{}(C_{12}H_4),\ C_2O_3$, &c. Such compositions as these do certainly not appear adapted to increase our confidence in the probability of this hypothesis on the constitution of the imides. Nevertheless, I consider it not impossible that these difficulties may be removed by future researches. A fresh investigation of this subject, which is yet so little exhausted, might perhaps lead to no uninteresting results.

Among the various hypotheses that may be advanced upon the chemical constitution of anisylic acid, and particularly for the explanation of the wonderful and manifold correspondence exhibited by anisylic acid and anisole on the one, and benzoylic acid and benzole on the other, as regards their chemical behaviour, none appears to me more simple or probable than the view expressed in the formulæ $HO.(C_{14}H_7O_2)\breve{}C_2,\ O_3$ (anisylic acid), and $(C_{14}H_7O_2)H$ (anisole); namely, that their combinations possess a chemical composition similar to that ascribed to benzoylic acid and benzole, and that they are only distinguished from the latter compounds in containing, instead of $C_{12}H_5$, the complex atom $(C_{14}H_7O_2)$. Objections may, perhaps, be raised as to the capability of the group $(C_{14}H_7O_2)$ of playing the part of a radical, and exercising functions similar to those of the adjunct $C_{12}H_5$ of benzoyl, or the carbohydrogen $C_{14}H_5$ in toluole, as assumed by this hypothesis. The following comparative table of corresponding anisyl- and benzoyl-compounds, and the corresponding bodies derived from both, will be best adapted to weaken any objections, made from a theoretical point of view, against the plausibility of the assumption that oxygen can be the constituent of an organic radical:

Anisyl.	Benzoyl.
$(C_{14}H_7O_2)\breve{}C_2$	$(C_{12}H_5)\breve{}C_2$
Anisylous acid.	Oil of bitter almonds.
$HO.(C_{14}H_7O_2)\breve{}C_2,\ O$	$HO.(C_{12}H_5)\breve{}C_2,\ O$
Anisylic acid.	Benzoylic acid.
$HO.(C_{14}H_7O_2)\breve{}C_2,\ O_3$	$HO.(C_{12}H_5)\breve{}C_2,\ O_3$

Chloranisylic acid.

$$HO \,.\, (C_{14} \left\{ \begin{matrix} H_6 \\ Cl \end{matrix} \right\} O_2) \frown C_2, O_3$$

Nitranisylic acid.

$$HO \,.\, (C_{14} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} O_2) \frown C_2, O_3$$

Dinoxybromide of anisyl.

$$(C_{14} H_7 O_2) \frown C_2, \left\{ \begin{matrix} O_2 \\ Br \end{matrix} \right.$$

Dinoxychloride of anisyl.

$$(C_{14} H_7 O_2) \frown C_2, \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} \right.$$

Dinoxamide of anisyl.

$$(C_{14} H_7 O_2) \frown C_2, \left\{ \begin{matrix} O_2 \\ NH_2 \end{matrix} \right.$$

Anisole.

$$(C_{14} H_7 O_2) H$$

Sulphanisolide.

$$(C_{14} H_7 O_2) \,.\, SO_2$$

Sulphanisole-sulphuric acid.

$$HO \,.\, (C_{12} H_7 O_2) \frown S_2, O_5$$

Nitranisole.

$$(C_{14} H_7 O_2) \,.\, NO_4$$

Dinitranisole.

$$(C_{14} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} O_2) \,.\, NO_4$$

Anisidine.

$$(C_{14} H_7 O_2) \,.\, NH_2$$

Nitranisidine.

$$(C_{14} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} O_2) \,.\, NH_2$$

&c.

Chlorobenzoylic acid.

$$HO \,.\, (C_{12} \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right) \frown C_2, O_3$$

Nitrobenzoic acid.

$$HO \,.\, (C_{12} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right) \frown C_2, O_3$$

Dinoxybromide of benzoyl.

$$(C_{12} H_5) \frown C_2, \left\{ \begin{matrix} O_2 \\ Br \end{matrix} \right.$$

Dinoxychloride of benzoyl.

$$(C_{12} H_5) \frown C_2, \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} \right.$$

Dinoxamide of benzoyl.

$$(C_{12} H_5) \frown C_2, \left\{ \begin{matrix} O_2 \\ NH_2 \end{matrix} \right.$$

Benzole.

$$(C_{12} H_5) H$$

Sulphobenzide.

$$(C_{12} H_5) \,.\, SO_2$$

Sulphobenzole-sulphuric acid.

$$HO \,.\, (C_{12} H_5) \frown S_2, O_5$$

Nitrobenzole.

$$(C_{12} H_5) \,.\, NO_4$$

Dinitrobenzole.

$$(C_{12} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right) \,.\, NO_4$$

Aniline.

$$(C_{12} H_5) \,.\, NH_2$$

Nitraniline.

$$(C_{12} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right) \,.\, NH_2$$

&c.

Independent of the proof which the above comparison appears to me to afford, that oxygenated organic radicals are capable of playing the part of ordinary radicals, consisting merely of carbon and hydrogen, I think that, after the assumption of secondary organic radicals, no doubt can exist on this subject. If the existence of hypothetical

radicals is assumed in the nitrophenylic acids, containing four, eight, and even twelve atoms of oxygen, we can have no hesitation in ascribing to the complex-atom ($C_{14}\,H_7\,O_2$) the properties of a radical. It is certainly difficult to conceive in what form the two equivalents of oxygen are contained in the adjunct of anisyl and the radical of anisole, anisidine, &c. One might imagine them to play a similar part to the two equivalents of chlorine, for instance, in dichlorobenzoylic acid: $HO\,.\,(C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right)\urcorner C_2,\,O_3$, or in dichloraniline: $(C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right)\,.\,NH_2$, assuming, therefore, the grouped atom ($C_{14}\,H_7\,O_2$) to be a secondary radical, derived from the primary one ($C_{14}\,H_9$). Such a substitution of 4 volumes of hydrogen by 2 volumes of oxygen is however in itself rather improbable, and unsupported, hitherto, by any data.

Many chemists consider anisole as a similar and homologous compound to hydrated oxide of phenyl (phenylic acid), from which indeed it differs only in containing $C_2\,H_2$ more. This view is supported particularly by the fact, that anisole is formed from anisylic acid under the same circumstances as hydrated oxide of phenyl is produced from salicylic acid, which is homologous to anisylic acid. This fact can, however, only be considered as a slight proof, as all other circumstances are favourable to the assumption that anisole possesses a constitution similar to benzole. Neither anisole nor its derivatives, dibromanisole or trinitranisole, possess the acid properties of phenylic acid, dibromophenylic acid, and trinitrophenylic acid. On the other hand, however, chrysanisic acid, lately discovered by Cahours,* which is formed, together with trinitranisole, by the action of fuming nitric acid upon anisylic acid, and is isomeric with trinitranisole, possesses exactly the properties which one would expect from a homologous combination corresponding to trinitrophenylic acid. There can be no hesitation in the decision of the question whether chrysanisic acid or trinitranisole is most nearly related to trinitrophenylic acid, since the first of the two possesses all, and the second none, of those properties so characteristic of trinitrophenylic acid. We are, moreover, acquainted with a substance isomeric to anisole, namely, kreosote, which appears at the same time to possess the greatest similarity to hydrated oxide of phenyl, to which it is at any rate much more closely related in its properties than to anisole, so that it may be assumed with some degree of probability, that kreosote and not anisole is the compound homologous to hydrated oxide of

* Ann. Ch. Phys. [3] XXVII, 454.

phenyl sought for. A farther support for this view is furnished by the boiling-points of these bodies. Hydrated oxide of phenyl boils at 187°, the homologous compound, containing $C_2 H_2$ more, should therefore boil, as usual, 19° higher, therefore at 206°. The boiling-point of kreosote approaches the latter number very closely, it being 203°, while anisole boils at as low a temperature as 152°. A similar regularity in the difference of boiling-points is likewise exhibited by anisole and its homologue phenetole (Cahours, loc. cit.) obtained by the distillation of salicylate of oxide of ethyl with caustic baryta, which has, according to Cahours, a boiling-point 20° higher than anisole (172°), and differs in its composition by an increase of $C_2 H_2$, and but slightly in its chemical behaviour from the latter substance.

Hydrated oxide of phenyl and kreosote are evidently the alcohols of the homologous radicals $C_{12} H_5$ and $C_{14} H_7$, the former being $HO . (C_{12} H_5) O$, the latter $HO . (C_{14} H_7) O$, hence, trinitrophenylic acid is composed according to the rational formula

$$HO . C_{12}\left\{\begin{matrix} H_2 \\ 3\,NO_4 \end{matrix}\right\} O,$$

and chrysanisic acid according to the formula

$$HO . C_{14}\left\{\begin{matrix} H_4 \\ 3\,NO_4 \end{matrix}\right\} O.$$

The following are the rational formulæ of the isomeric combinations in question, together with those of the members as yet unknown:

$\underbrace{HO . (C_{12} H_5) O}$ Hydrated oxide of phenyl.

$\underbrace{HO . (C_{12}\left\{\begin{matrix} H_2 \\ 3\,NO_4 \end{matrix}\right\}) O}$ Trinitrophenylic acid.

$\underbrace{(C_{12} H_5 O_2) H}$ Unknown.

$\underbrace{(C_{12}\left\{\begin{matrix} H_3 \\ 2\,NO_4 \end{matrix}\right\} O_2) . NO_4}$ Unknown.

$\underbrace{HO . (C_{14} H_7) O}$ Kreosote.

$\underbrace{HO . (C_{14}\left\{\begin{matrix} H_4 \\ 3\,NO_4 \end{matrix}\right\}) O}$ Chrysanisic acid.

$\underbrace{(C_{14} H_7 O_2) H}$ Anisole.

$\underbrace{(C_{14}\left\{\begin{matrix} H_5 \\ 2\,NO_4 \end{matrix}\right\} O_2) . NO_4}$ Trinitranisole.

$$\underbrace{HO \,.\, (C_{16}\, H_9)}_{\text{Unknown.}}\, O \qquad\qquad \underbrace{HO \,.\, (C_{16}\left\{\begin{matrix} H_6 \\ 3\, NO_4 \end{matrix}\right.)}_{\text{Unknown.}}\, O$$

$$\underbrace{(C_{16}\, H_9\, O_2)\, H}_{\text{Phenetole.}} \qquad\qquad \underbrace{(C_{16}\left\{\begin{matrix} H_7 \\ 2\, NO_4 \end{matrix}\right\} O_2) \,.\, NO_4}_{\text{Trinitrophenetole.}}$$

It can scarcely be considered doubtful, that salicylic and salicylous acids correspond in their rational composition to anisylic and anisylous acids:

Salicylic acid . . .	$HO \,.\, (C_{12}\, H_5\, O_2)\frown C_2,\, O_3$
Salicylous acid . .	$HO \,.\, (C_{12}\, H_5\, O_2)\frown C_2,\, O$
Anisylic acid . . .	$HO \,.\, (C_{14}\, H_7\, O_2)\frown C_2,\, O_3$
Anisylous acid . .	$HO \,.\, (C_{14}\, H_7\, O_2)\frown C_2,\, O$

and that the hydrogen-combination of the radical $(C_{12}\, H_5\, O_2)$ isomeric with hydrated oxide of phenyl, will likewise be discovered. The difference in the behaviour of salicylic and anisylic acids, when heated with baryta, is certainly highly deserving of attention; it is, however, not more strange than many other reactions in which homologous combinations so frequently differ from each other.

Since Hofmann's researches on methylaniline, diethylamine, &c., have taught us that the ether-radicals can replace hydrogen in organic combinations, I consider the existence of a compound similar and analogous to anisole, having the rational formula $(C_{12}\, H_5\, O_2) \,.\, (C_2\, H_3)$, as not improbable. It is possible that the anisole obtained from salicylate of oxide of methyl may possess such a composition: $(C_2\, H_3\, O) \,.\, (C_{12}\, H_5\, O_2)\frown C_2,\, O_3 + 2\, BaO = (C_{12}\, H_5\, O_2) \,.\, (C_2\, H_3) + 2\, (BaO \,.\, CO_2)$, and that, as it differs probably but little from the anisole prepared from anisylic acid: $(C_{14}\, H_7\, O_2)\, H$, these slight differences have been overlooked.

If formobenzoic acid may be considered as a double-compound of oil of bitter almonds and formic acid, its isomerism with anisylic acid and gaultheric acid, may be easily explained by their different rational formulæ:

$HO \,.\, (C_{14}\, H_7\, O_2)\frown C_2,\, O_3$	Anisylic acid.
$(C_2\, H_3)\, O \,.\, (C_{12}\, H_5\, O_2)\frown C_2,\, O_3$	Gaultheric acid.
$HO \,.\, H\frown C_2,\, O_3$; $HO \,.\, (C_{12}\, H_5)\frown C_2,\, O$	Formobenzoic acid.

The following rational formulæ afford, likewise, an explanation of

the isomerism of the four combinations, composed according to the empirical formula: $C_{14}\,H_7\,NO_4$:

Salicylamide	$(C_{12}\,H_5\,O_2)\overset{\frown}{}C_2, \left\{\begin{matrix}O_2\\NH_2\end{matrix}\right.$
Nitrotoluole	$(C_{14}\,H_7)\,.\,NO_4$
Benzamic acid . .	$HO\,.\,(C_{12}\left\{\begin{matrix}H_4\\NH_2\end{matrix}\right.)\overset{\frown}{}O_3$
Anthranilic acid (carbanilic acid) . . .	$HO\,.\,C\left\{\begin{matrix}O\\And\end{matrix}\right.; CO_2$.*

By these formulæ, the chemical character of each individual compound is so definitely expressed, that a cursory examination thereof is sufficient to enable us to understand, for instance, why salicylamide yields, upon being heated with potassa, ammonia, and not aniline; why anthranilic acid yields, under similar circumstances, neither salicylic acid nor ammonia, but carbonic acid and aniline; and why benzamidic acid, without being identical with anthranilic acid, yields the same products:

$$\underbrace{HO\,.\,C\left\{(C_{12}\,\begin{matrix}O\\H_4\end{matrix})\supset NH_2\right\}; CO_2}_{\text{Anthranilic acid.}} + 2\,KO = \underbrace{(C_{12}H_5)\,.\,NH_2}_{\text{Aniline.}} + 2\,(KO\,.\,CO_2)$$

$$\underbrace{HO\,.\,(C_{12}\left\{\begin{matrix}H_4\\NH_2\end{matrix}\right.)\overset{\frown}{}C_2, O_3}_{\text{Benzamidic acid.}} + 2\,KO = \underbrace{(C_{12}\,H_5)\,.\,NH_2}_{\text{Aniline.}} + 2\,(KO\,.\,CO_2)$$

I have, in the foregoing, endeavoured to show, by a series of examples, how easily the facts, which appeared hitherto incompatible with the radical-theory, and have been principally employed, by the opponents of this theory as arguments against the existence of compound radicals, may be made to accord with the above theory, as soon as the idea of the immutability of these radicals is set aside, and exchanged for the opinion that they are complex atoms, in which certain atoms may be substituted by others. I have also endeavoured to establish the view that new secondary radicals are thus produced, many of which still possess properties similar to those of the primary ones; that, however, not all radicals are equally adapted for conversion into secondary radicals (*e. g.* ethyl being less so than acetyl); that indeed one and the same radical, according to the manner in which it is combined, possesses this property in different degrees (ethyl, for instance, possesses it to a higher degree in the compound

* And = $(C_{12}\,H_4)\supset NH_2$ (anilide).

ethers, than it does in the simple ones). Lastly, I have deemed it necessary to distinguish between two classes of organic radicals, the true repetitions (analogues) of hydrogen (the ether-radicals), and the conjugate radicals, in which the former exist as adjuncts, for instance, of C_2, As, Sb, Sn, &c. Besides these, there appears to exist a third class, formed by the combination of homologising carbohydrogens: $C_2 H_2$, and similar compounds with simple substances, for instance, with C_2 in the radical of succinic acid, with Pt in elayl-platinum, &c., and which may, therefore, be viewed as homologues of these elements.

The question still remains to be answered, whether and how the assumption of alterable chlorinated radicals can be made to accord with the electro-chemical theory. According to this theory, the nature of a chemical combination is dependent on that of its constituents, and hence the substitution of the negative chlorine for the positive hydrogen would be impossible. It appears to me necessary, before all, to examine carefully whether the hydrogen, replaceable by chlorine, really is the electro-positive constituent of the radicals, and whether the chlorine, which exercises the functions of hydrogen, retains the negative properties generally ascribed to it.

In simple inorganic combinations, it is in most cases easy to determine which element is the positive, and which the negative constituent, but in organic compounds it is much more difficult to decide this question.—Berzelius adhered to the rule "that the application of what is, and will still become known with respect to the mode of combination of the elements in inorganic nature, serves as a guide for the proper judgment of their combinations in organic nature, by which we may hope to arrive at correct and concordant conceptions of the mode of composition of those bodies which are produced under the influence of vital processes, as also of those which are produced by the metamorphoses of these bodies by chemical means." This principle led to the hypothesis, that organic combinations must contain compound radicals, exercising therein functions similar to those of simple radicals in inorganic nature, and that in such a complex atom, playing the part of a simple radical, electro-positive properties are predominant, as in the latter, by which the combination with the negative elements is effected; no farther point of view is however furnished us by this hypothesis, from which to arrive at a decision of the question, which electro-chemical properties are possessed by the elements composing those groups of atoms, as there is no analogy in inorganic chemistry with regard to this point.

We must, therefore, content ourselves at present with the conviction, that there were in the elements constituting organic radicals, electrical oppositions at the time of their combination, as required by the electro-chemical theory, and must leave it to the future to discover by other means which of those constituents are the positive, and which the negative ones. Even in the single and most simple case, in which two elements, carbon and nitrogen, combine directly to form an organic radical, it is quite out of our power to determine, with any degree of probability, to which of the elements cyanogen owes its predominant negative properties, and whether the nitrogen or carbon constitutes the positive (with respect to the negative) constituent. The solution of these questions becomes much more difficult, with reference to the radicals consisting of carbon and hydrogen, which are produced under far more complicated circumstances, and cannot be formed, like cyanogen, directly from their elements.

In this difficulty, the phenomena of substitution afford appropriate means with which, at any rate, to impart some probability to the conjecture, that the hydrogen, for instance, in acetyl, is possessed of electro-chemical capacities differing from that contained in water, or hydrochloric acid. We are also justified in doubting that the chlorine entering acetyl or aniline in the place of hydrogen, carries with it the powerful electro-negative properties of which it is possessed in its inorganic combinations. It can, indeed, be no longer doubted that, in the simple substances, the direction of the powers of affinity peculiar to them in their so-called normal state, is altered under certain circumstances, and frequently by apparently unimportant causes, and that, therefore, they assume at times an electro-chemical character differing from that they usually possess. The red amorphous phosphorus, produced by heating phosphorus to 240° C., is certainly still the same substance, but, with respect to its chemical properties, it is quite a different body. This element, most remarkable, next to the alkali-metals, for its affinity for oxygen, possesses, singularly enough, after exposure to the requisite heat, not a trace of this affinity. The red phosphorus differs so perfectly from the normal phosphorus in its physical properties, and in the altered direction of its powers of affinity, that if its relations to colourless phosphorus were unknown, it would certainly be considered as a new element.

These facts appear to me to warrant the assumption that hydrogen *may* also exist in organic combinations in a state, in which it is possessed of properties differing from those of the ordinary electro-

positive element. Does not hydrogen exhibit a great difference, with regard to its affinities, in the free and the nascent state? In the same manner, I consider it not impossible that the chlorine, entering into the place of hydrogen, in compound radicals, assumes, by this act of substitution, a less negative character than that peculiar to it in its normal state. It would not, according to this, be the positive hydrogen and the negative chlorine, bromine, &c., that replace each other, but bodies differing perhaps no more in their electro-chemical properties than oxygen and sulphur.

This mode of viewing evidently still exhibits great deficiencies, it shows however, at any rate, that it is not impossible to make the enigmatical phenomena of substitution accord with the radical-theory. "A good theory," as Hofmann* very aptly remarks, "is more than a *temporary* expression of the state of science collecting under a general view the facts acquired up to the moment of its birth. It must not like ephemeral hypothesis, vanish before the light of succeeding discoveries, but expanding with the growth of science, it must still correctly represent the known facts, though of necessity modified into a more general expression."

Who could doubt that the radical of theory is capable of such an expansion? If the conception hitherto adopted of the immutability of organic radicals be only done away with, the explanation of the phenomena of substitution will present no farther difficulties. It would be ridiculous to allow a single fact, difficult of explanation, to induce us to throw aside at once a theory which has served us for so long a period as a trustworthy guide in the difficult field of organic chemistry, and has preserved us most securely from the errors of a code of laws like that which has been laid down by Laurent and Gerhardt—unless indeed we had some better theory to substitute for it. The radical-theory has already outlived the theory of metalepsy and the theory of types, of which at the present time scarcely mention is made in the researches of French chemists; the nucleus-theory and the ingeneous invention of whole numbers of atoms will likewise disappear as rapidly from the field; for chemistry is indeed something better than a mere arithmetical problem, into which Laurent and Gerhardt endeavour to convert it.

By founding the hypothesis, that replacements of hydrogen by chlorine, hyponitric acid, &c., occur in compound radicals, the question, whether oxygen can constitute the component of a radical is likewise answered. It is easy to render to oneself an account of the form in which oxygen exists in the radicals of nitrobenzoic and

* Phil. Trans. 1851, I, 96.

nitrophenylic acids; in many other cases, as in anisyl, salicyl we are as yet unable to do so, and must therefore content ourselves for the present with the establishment of the mere fact. Perhaps these are also secondary radicals, which we have not as yet been able to trace back to their primary ones.

Since Frankland succeeded in isolating from their combinations the ether-radicals, ethyl and amyl, to which are added the radicals, methyl and valyl, obtained by the electrolysis of acetic and valeric acids, various opinions have been put forward and supported with regard to the nature of these carbohydrogens, and of these the view, that they are not the true radicals, but isomeric modifications of them, appears to have become the one most generally entertained. According to Laurent and Gerhardt, they possess double the atomic weight ascribed to them by Frankland and myself, because the formulæ $C_2 H_3$, $C_4 H_5$, &c., are at variance with their law of whole numbers of atoms. I acknowledge that it is not in my power to follow these chemists in their train of argument. The circumstance that none of these radicals re-combines directly with oxygen, chlorine, sulphur, &c., to form simple ethers, is however more deserving of attention. The importance attached to this circumstance is the greater, because other radicals, particularly kakodyl, enter with such facility into combination with the above-named metalloids; upon this circumstance, endeavours have been made to establish the view, that these indifferent carbohydrogens are not the true radicals contained in the ethers.

It is a tolerably general, but certainly unfounded opinion, that the organic radicals, in the free state, must be gifted with powerful affinities. Many have expected, particularly of the ether-radicals, that their properties would not be much unlike those of potassium. This prejudice has evidently originated with the great difficulties hitherto met with in the isolation of the ether-radicals from their combinations. This is, however, at present effected in the most simple manner; and since, contrary to expectations, methyl, ethyl, amyl, &c., differ much in their combining powers, from potassium as well as from kakodyl, one is too much inclined to regard their indifferent properties as the most certain proof that they are not the ether-radicals. Those who argue thus, forget that hydrogen and platinum also belong to the radicals, and that these two substances exhibit just as little tendency to combine directly with oxygen, chlorine, &c., without the mediating influence of another agent. Nothing justifies us in classing the ether-radicals with potassium; on the other hand, it appears to me quite natural to compare them with

hydrogen, as a repetition of which they must be regarded. In fact, they differ no farther in their properties from the latter, than is conditional upon their mere complex composition. Hydrogen and methyl both possess, under ordinary circumstances, no affinity for oxygen, iodine, sulphur, &c.; when mixed with chlorine in the dark, they both remain unaltered, combination only ensues under the influence of light. It is, however, no more strange that chloride of methyl is not formed under these circumstances, which the analogy with hydrogen would lead us to expect, than that, on igniting a mixture of methyl-gas and oxygen, no oxide of methyl, but water, &c., is formed. It is easily conceivable, that the stronger affinities of oxygen and chlorine for the constituents of methyl must predominate, as is the case, likewise, when kakodyl is brought together with free oxygen or chlorine.

The deficiency exhibited by the ether-radicals in strong powers of affinity does not therefore appear to me any reason whatever, why they should be excluded from the series of radicals; in that case, hydrogen must also not be allowed to stand as a radical. And, finally, the circumstance, that kakodyl, zincethyl, stibethyl, and, as may be predicted with tolerable certainty, even acetyl, the lower oxide of which, aldehyde, possesses so powerful an affinity for oxygen, are much more nearly related to the alkali-metals, as regards their powers of combination, cannot be regarded as a rule for the ether-radicals, as these possess a constitution totally different from the above conjugate radicals.

The principal support for the view extensively entertained, that methyl, ethyl, butyl, amyl, and capryl, in the isolated state, possess double the atomic weight assigned to them, that therefore their composition should be expressed by the empirical formulæ $C_4 H_6$ (methyl), $C_8 H_{10}$ (ethyl), $C_{16} H_{18}$ (butyl), $C_{20} H_{22}$ (amyl), $C_{24} H_{26}$ (capryl), is found in the circumstance to which attention was first called by Hofmann, that the boiling-points of butyl, amyl, and capryl, differ from each other successively by 40°, on account of the difference in their composition of $2\ C_2 H_2$, while, if they were composed according to the formulæ $C_8 H_9$, $C_{10} H_{11}$, $C_{12} H_{13}$, their boiling-points would only differ successively 20°. This observation appears to me worthy of the greatest attention; I cannot, however, consider it as decisive. Hofmann himself, by the discovery of the methylated and ethylated aniline-bases, has brought to light facts which rob the assumption that the boiling temperatures of organic combinations increase 20° for every additional $C_2 H_2$ of its general validity. As the boiling-points of those aniline-bases increase almost regularly by only

10°, instead of 20°, for every equivalent of $C_2 H_2$ added to the aniline, the difference of $C_2 H_2$ in the ether-radicals may likewise just as easily effect a difference of 40° in the boiling-point.

The question, whether these carbohydrogens are the real ether-radicals, or merely isomeric combinations, appears to me, at any rate, to be of but little importance with respect to the radical-theory. They may be shown, by future researches, to be combinations of a different nature, without endangering the radical-theory in the slightest degree. In the present state of science, however, the preference must undeniably be given, for its greater simplicity, to the assumption of the identity of those carbohydrogens with those of the radicals hypothetically assumed in the ethers.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 20, 1851.

THOMAS GRAHAM, Esq., V.P., in the Chair.

M. Balard was elected a Foreign Member of the Society.

The following presents were announced:

"The Pharmaceutical Journal for January:" presented by the Editor.

"The Journal of the Franklin Institute:" presented by the Institute.

"Silliman's American Journal of Science and Arts for September, 1850:" presented by the Editor.

"The Art Union of London Almanac for 1851:" presented by the Publisher.

The following papers were read:

1. "On the Magnetism of the Elementary Bodies, and their Binary Compounds:" by Mr. Richard Adie.
2. "Analysis of the Water of the Artesian Well at Southampton:" by J. Robson, Esq., of Queenwood College.
3. "On the Selenocyanides:" by William Crookes, Esq., of the Royal College of Chemistry.

February 3, 1851.

WILLIAM ALLEN MILLER, M.D., V.P., in the Chair.

The following presents were announced:

"The Pharmaceutical Journal for February:" presented by the Editor.

"The Journal of the Franklin Institute for December, 1850:" presented by the Institute.

"The Annual Reports of the Royal Cornwall Polytechnic Society from 1835—1849:" presented by the Society.

"Boerhaaves' Chemistry, 3rd Edition, 1753:" presented by Mr. H. Sugden Evans.

The following papers were read:

1. "On the Composition of certain Well-waters in the neighbourhood of London, with some observations on their action on lead:" by Henry Noad, Esq., Lecturer on Chemistry at St. George's Hospital.
2. "Observations on the Deportment of Diplatosamine with Cyanogen:" by G. B. Buckton, Esq., F.L.S.

February 17, 1851.

RICHARD PHILLIPS, ESQ., President, in the Chair.

The following memoirs and journals were presented:

"On the condition of certain Elements at the moment of Chemical Change, by Benjamin Collins Brodie, Esq.": by the Author.

"On the Chemical Constitution of the Rocks of the Coal Formation, by Hugh Taylor, Esq.": by Dr. Anderson.

"On the Optical Properties of a compound of Iodine and Codeine, by William Haidinger, Esq.": by Dr. Anderson.

"On a remarkable compound of Iodine and Codeine, by Thomas Anderson, M.D., F.R.S.E.": by the Author.

"Silliman's American Journal of Science and Art for January, 1851:" by the Editor.

"The Quarterly Journal of the Geological Society for February, 1851:" by the Society.

The following paper was read:

"On the Explosive Compound usually denominated Iodide of Nitrogen: by Dr. J. H. Gladstone."

March 3, 1851.

RICHARD PHILLIPS, ESQ., President, in the Chair.

Astley Paston Price, Ph. D., and William J. Russell, Esq., were elected Fellows of the Society.

The following presents were announced:

"The Pharmaceutical Journal for March:" by the Editor.

"The Journal of the Franklin Institute for January:" by the Institute.

"Fourth Report on the Analysis of the Ashes of Plants, by J. Thomas Way and G. W. Ogston, Esqrs.": by the Authors.

"Miscellaneous Results from the Laboratory, by J. Thomas Way, Esq.": by the Author.

The following paper was read:

"On the Combination of Arsenious Acid and Albumen, and remarks on Liebig's Theory:" by Sheridan Muspratt, Ph. D.

March 17, 1851.

RICHARD PHILLIPS, ESQ., President, in the Chair.

Montague Lyon Phillips, Esq., and David Gambre, Esq., were l ected Fellows of the Society.

The following presents were announced:

"Experimental Researches in Electricity, series 22 — 27, by Michael Faraday, D.C.L.": by the Author.

"The Literary Gazette for January and February:" by the Editor.

"A Letter to the Right Hon. Sir George Grey, Bart., M.P., on Medical Registration, and the present condition of the Medical Corporations, by Emeritus": by the Author.

"Head Juries of the Exhibition of 1851:" by Dr. Lyon Playfair.

A paper was read by Professor Clark on the Chemical Examination of Waters.

NOTICES

OF

PAPERS CONTAINED IN THE

"Philosophical Translations" and Foreign Journals.

By Henry Watts, B.A., F.C.S.

On the Diffusion of Liquids.*

By Professor Graham, F.R.S., F.C.S.

The experiments described in the author's former paper on this subject furnished strong grounds for believing that isomorphous salts possess a similar diffusibility. All the salts of potash and ammonia, which were compared, appeared to be equi-diffusive; so also were the salts of certain magnesian bases. A single preliminary observation on the nitrates of lead and baryta, however, opposed the general conclusion, and demanded further inquiry. It is scarcely necessary to say that any new means of recognising the existence of the isomorphous relation between different substances, must prove highly valuable. Let us inquire therefore how far liquid diffusion is available for that purpose.

The salts were still diffused from weak solutions, that is from solutions containing from 1 to 8 per cent of salt; but now a measure of the solution, equal to 100 grs. of water, was made to contain 1 grain of the salt, to form what is called the 1 per cent solution, instead of 1 grain of salt being added to 100 grs. of water, as before, without reference to the condensation which generally occurs. The quantities 1, 2, 4 and 8 per cent thus indicate the parts of salt present in a constant volume of liquid,—as 10, 20, 40 and 80 grs. of the salt in 1000 water grain-measures of the solution. The same phials for the solution and jars for the external water-atmosphere continued to be used, and the manipulations were similar. It is believed, however, that the temperature of the liquids was maintained more uniform in the new experiments than the old, partly by the better regulation of the temperature of the apartment, and partly by placing the jars close together upon a table with upright ledges, and covering the whole

* Philosophical Transactions 1850, p. 805.

over with sheets of paper during the continuance of an experiment. The mass of fluid in 80 or 100 jars, which were employed at once and placed together, made the small oscillations of temperature, which might still occur, slow and less injurious.

The investigation is also extended to several new substances, such as hydrocyanic acid, acetic acid, sulphurous acid, alcohol, ammonia and salts of organic bases, without reference to isomorphous relations. It is very necessary to have data which are minute and accurate respecting the diffusion of a considerable variety of substances. This it is the object of the present investigation to endeavour to supply, leaving speculative deductions in general respecting the nature and laws of liquid diffusion for a future occasion.

The density of all the solutions was observed at a constant temperature, namely, 60° Fahr.

1. *Hydrochloric acid.*—The period of diffusion arbitrarily chosen for this acid was five days. The diffusate, or quantity of acid diffused, was determined by precipitating the liquid of the external reservoirs with nitrate of silver, and weighing the chloride of silver formed. In the 1 and 2 per cent solutions, the liquids of two jars were generally mixed and precipitated together.

The number of cells diffused at once, unless otherwise specified, was always eight cells, of the 1 and 2 per cent solutions, and four cells of the 4 and 8 per cent solutions. In this abstract the means only of these experiments are given.

The diffusates at the same temperature were found to be as follow:

Diffusion in five days at 51° Fahr.; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·41	0·97
From 2 per cent solution . . .	15·04	2·00
From 4 per cent solution . . .	30·72	4·08
From 8 per cent solution . . .	67·68	9·00

The 2 per cent solution is taken as the standard of comparison for the ratios, instead of the 1 per cent solution, from the greater accuracy with which the diffusion of the former can be observed.

The increasing diffusibility with the larger proportions of acid here observed is unusual, at least in the degree exhibited by the 8 per cent solution. Other substances, as will be immediately observed of nitric acid, appear to lose proportionally in diffusibility as their solutions are concentrated.

Hydrochloric acid belongs to the most diffusive class of substances known; it appears to exceed hydrate of potash at 53°·5, as 7.56 to 6·12, or as 100 to 80·9*.

* Phil. Trans. 1850, 39.

The rapidity with which hydrochloric acid diffuses, and the facility with which that substance may be estimated, induced the author to examine the progression with which its diffusion takes place with increasing times in a minute manner. The 2 per cent solution was diffused for times increasing by six hours, from twelve hours or 0·5 day to 4·75 days, six cells being diffused for every period. Instead of determining the acid diffused separately in each jar or pair of jars, the contents of the six jars of each experiment were mixed together, and a definite proportion of the liquid precipitated by nitrate of silver, and the chloride of silver weighed, so as to obtain at once the mean result. Another observation for 5·75 days is added, although made at a sensibly higher temperature.

DIFFUSION OF HYDROCHLORIC ACID, 2 PER CENT SOLUTION; ONE CELL.

Time.	Temperature.	Diffusate in grains.	Differences.
days.	°		
0·5	53·75	0·909	
0·75	53·75	1·312	·403
1	53·75	1·766	·454
1·25	53·75	2·353	·587
1·5	53·75	2·596	·243
1·75	53·58	3·178	·582
2	53·58	3·410	·232
2·25	53·42	3·967	·557
2·5	53·58	4·339	·372
2·75	53·50	4·618	·279
3	53·50	4·969	·351
3·25	53·50	5·304	·335
3·5	54·85	5·857	·553
3·75	54·85	6·254	·397
4	54·85	6·407	·153
4·25	54·85	6·795	·388
4·5	54·71	7·034	·239
4·75	54·71	7·473	·339
5·75	56·46	8·363	

The differences are evidently affected by accidental errors of observation. The diffusion in 3·5 days is also increased by a rise of temperature of more than 1° in that and the following experiments. The diffusion always increases with the time, but less rapidly, according to a gradually diminishing progression.

Hydriodic acid.—Time of diffusion five days, as for hydrochloric acid. The acid diffused was estimated from the weight of iodide of silver which it gave when precipitated by nitrate of silver.

Diffusion from 2 per cent solutions at 51° Fahr.

Hydrochloric acid . . .	15·04	100
Hydriodic acid	15·11	100·46

These experiments indicate a similarity of diffusion between the two isomorphous substances, hydrochloric and hydriodic acids.

Hydrobromic acid.—Time of diffusion five days. The diffusate was estimated from the bromide of silver.

Diffusate from 2 per cent solutions at 59°·7 Fahr.

Hydrochloric acid . . .	16·55	100
Hydrobromic acid . . .	16·58	100·18

Hydrobromic acid appears therefore to coincide in diffusibility with hydrochloric acid at this temperature. It may be remarked that these three acids, hydrochloric, hydrobomic and hydriodic, do not exhibit the same correspondence in another physical property, namely, the densities of their aqueous solutions containing the same proportion of acid. The densities of 2 per cent solutions of hydrochloric and hydriodic acids appear to be respectively 1·0104 and 1·0143, at 60° Fahr., and that of hydrobromic acid is an intermediate number. The same acids are also known to differ considerably in the boiling-points of solutions containing the same proportion of acid. A considerable diversity of physical properties appears here to be compatible with equal diffusibility in substances which are isomorphous.

Bromine.—Pure water readily dissolves more than 1 per cent of this substance. The solution prepared, however, contained only 0·864 per cent of bromine, as was ascertained by treating it with sulphurous acid and afterwards precipitating by nitrate of silver. Its density was 1·0070. It was evident, from the slow appearance of the brown colour in the exterior cell, that bromine diffuses less rapidly than hydrobromic acid.

The diffusion-time of bromine was made ten days, or double the time of hydrobromic acid. Two cells contained together a diffusate of 5·80 grs. of bromine; another two cells a diffusate of 5·88 grs.; mean 5·84 grs. at 60°·1 Fahr.; or 6·76 grs. for a 1 per cent solution. Doubling the last result we have 13·52 grs. for a 2 per cent solution, which is still considerably under the diffusate of hydrobromic acid (16·58 grs.) in half the time.

3. *Hydrocyanic acid.*—Time of diffusion five days. The acid diffused was estimated from the cyanide of silver which it gave with nitrate of silver.

Hydrocyanic acid, 1·766 per cent, made up to a density of 1·0142 with sulphate of potash. Diffused at 64°·2, in six cells, 11·40, 11·86, 11·80; mean 11·68 grs. for two cells. Calculated for 2 per cent, 13·23 grs. at 64°·2 in two cells, or about 13·10 grs. at 62°·8,

assuming this acid to be affected in the same way by temperature as hydrochloric acid.

Hydrocyanic acid here appears less diffusive than hydrochloric acid, at the same temperature 62°·8, as 13·10 to 16·40, or as 79·6 to 100, and not to belong therefore to the same class of diffusive substances.

4. *Nitric acid.*—Time of diffusion five days. The quantity of this acid diffused was always determined with great exactness by neutralization by means of a normal solution of carbonate of soda.

The diffusion of the different proportions of this acid at one temperature is as follows:

Diffusion of nitrate of water in five days at 51°·2; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·99	0·95
From 2 per cent solution . . .	14·74	2
From 4 per cent solution . . .	28·76	3·90
From 8 per cent solution . . .	57·92	7·86

The usual approach to equality of diffusion, between chlorides and nitrates, is observable in hydrochloric and nitric acids, at least in the 1 and 2 per cent solutions.

Diffusion from 1 per cent solution at 53°·5.

Hydrochloric acid	7·56	100
Nitrate of water	7·28	96·3

Diffusion from 2 per cent solution.

Hydrochloric acid at 51°	15·04	100
Nitrate of water at 51°·2	14·74	98·0

The 2 per cent solutions of both acids were also diffused at higher temperatures.

Diffusion from 2 per cent solution.

Hydrochloric acid at 62°·8	16·46	100
Nitrate of water at 63°·2	16·76	101·8

Here the diffusibility of the two acids is as nearly as possible equal.

Diffusion from 4 per cent solution.

Hydrochloric acid at 51°	30·72	100
Nitrate of water at 51°·2	28·76	93·7

Diffusion from 8 per cent solution.

Hydrochloric acid at 51°	67·68	100
Nitrate of water at 51°·2	57·92	85·3

The wide divergence between these two acids, in the 8 per cent

solution, is produced by the remarkably increased diffusion of hydrochloric acid in that high proportion.

5. *Sulphuric acid.*—That time of diffusion arbitrarily chosen for this acid was ten days. The diffusate of this acid was determined in the same manner as that of nitric acid.

The diffusion of the different proportions of sulphuric acid is as follows:—

Diffusion of sulphate of water in ten days at 49°·7; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	8·69	1·03
From 2 per cent solution . . .	16·91	2
From 4 per cent solution . . .	33·89	4·01
From 8 per cent solution . . .	68·96	8·16

The diffusibility of different strengths of this acid appears to be pretty uniform, but with a slight tendency to increase in the higher proportions, like hydrochloric acid.

Sulphuric acid is inferior in velocity of diffusion to hydrochloric acid, but still appears to possess considerably more than half the diffusibility of the latter.

6. *Chromic acid.*—Time of diffusion ten days. The diffusates from four cells of the 2 per cent solution were mixed together, and the quantity of chromic acid diffused for two cells reduced by means of hydrochloric acid and alcohol, and weighed as oxide of chromium.

1·762 per cent of anhydrous chromic acid, density 1·01404, diffused at 67°·3, gave 19·78 grs. of chromic acid in two cells. Calculated for 2 per cent, 22·43 grs. of chromic acid, in two cells, at 67°·3. The diffusion of sulphuric acid at 63°·5, was 19·73 grs., which would give about 21 grs. of that acid at 67°·3.

7. *Acetic acid.*—Time of diffusion ten days. This acid cannot be determined accurately by the acidimetrical method, owing to the acetates of potash and soda being essentially alkaline to test paper, like the carbonates of the same bases, although neutral in composition. The weight of carbonate of baryta dissolved by the acid was had recourse to.

Diffusion of acetate of water in ten days at 48°·8; two cells.

	Grs.	Ratio.
From 2 per cent solution . . .	11·31	2
From 4 per cent solution . . .	22·02	3·83
From 8 per cent solution . . .	41·80	7·26

The diffusibility diminishes with the larger proportions of acid. This acid appears to be considerably less diffusive than sulphuric acid. I was led to over-estimate the diffusion of acetic acid in a preliminary

observation of my former paper, by trusting to the acidimetrical method of determination. Hydrochloric acid appears to diffuse about two and a half times more rapidly than acetate of water, at the same temperature.

8. *Sulphurous acid.*—The time of diffusion chosen for this acid was ten days, for comparison with sulphuric acid. The usual number of eight cells of the 1 and 2 per cent solutions were diffused, and four cells of the 4 and 8 per cent solutions. The whole diffusates of each proportion were then mixed together, and the proportional quantity of liquid representing two cells in the 1 and 2 per cent solutions, and 1 cell in the 4 and 8, was converted into sulphuric acid by a slight excess of bromine, and determined from the sulphate of baryta.

Diffusion of sulphurous acid in ten days at 68°·1 ; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	8·09	0·954
From 2 per cent solution . . .	16·96	2
From 4 per cent solution . . .	33·00	3·821
From 8 per cent solution . . .	66·38	7·827

This substance appears to be less diffusive than sulphuric acid at the same temperature; the diffusion of sulphurous acid at 68°·1 considerably resembles that of sulphuric acid at 49°·7.

9. *Ammonia.*—The time of diffusion chosen was 4·041 days, or that of hydrate of potash with chloride of sodium at seven days. The whole diffusates of each proportion were mixed together, and the quantity of ammonia diffused for two cells determined by an alkalimetrical experiment, which was always repeated twice. It was necessary for diffusion to have the ammoniacal solution made denser than water, which was effected by the addition of common salt.

Diffusion in 4·04 days at 63°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	4·93	1·029
From 2 per cent solution . . .	9·59	2
From 4 per cent solution . . .	19·72	4·117
From 8 per cent solution . . .	41·22	8·605

Ammonia appears to have a diffusibility approaching to that of hydrate of potash. It appears somewhat less diffusive than hydrocyanic acid at the same temperature, in the proportion of 12 to 13 nearly; or to possess about three-fourths of the diffusibility of hydrochloric acid.

10. *Alcohol.*—Time of diffusion ten days. The quantity of alcohol diffused was determined by careful distillation.

Diffusion in ten days at 48°·7; two cells.

From 2 per cent solution	8·62
From 4 per cent solution	16·12
From 8 per cent solution	35·50

It would be unsafe to draw any conclusion as to the proportionality of the diffusion of alcohol to the strength of the solution from these experiments.

Alcohol does not appear to belong to the same class of diffusive substances as acetic acid, which might be expected from their similarity of composition, but possesses a considerably lower diffusibility.

Diffusion from 2 per cent solutions in ten days.

Acetate of water at 48°·8 . .	11·51	100
Alcohol at 48°·7	8·62	74·9

The diffusion of alcohol approaches to one-half of that of sulphate of water, at nearly the same temperature.

Alcohol may be substituted for water to dissolve certain salts, and also as an atmosphere into which these salts may diffuse. From experiments which have been commenced on this subject, it appears that the diffusion of hydrate of potash, iodide of potassium, chloride of calcium and others is about four times slower in alcohol of density 0·840 than in water. The salts likewise often exhibit the same relations in their diffusibility in alcohol, as in water, with some singular exceptions, such as chloride of mercury.

11. *Nitrate of baryta.*—Time of diffusion 11·43 days.* The salt diffused was precipitated by sulphuric acid, and calculated from the weight of the sulphate of baryta formed.

Diffusion in 11·43 days at 64°·1; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·72	1·026
From 2 per cent solution . . .	15·04	2
From 4 per cent solution . . .	29·60	3·936
From 8 per cent solution . . .	54 50	7·247

12. *Nitrate of strontia.*—Time of diffusion 11·43 days. Of anhydrous nitrate of strontia 0·82 per cent; density 1·0063. Diffused at 51°·5, in eight cells, 5·59, 5·62, 5·44, 5·69; mean 5·59 grs. for two cells; calculated for 1 per cent, 6·79 grs. at 51°·5 for two cells.

The diffusion of nitrate of strontia almost coincides with that of the isomorphous nitrate of baryta at the same temperature.

* This time is to that of sulphate of magnesia (16·166 days) as the square root of 8 is to the square of 16; but does not appear to express the true relation between these salts.

Diffusion from 1 per cent solutions at 51°·5 in 11·43 days.

Nitrate of baryta	6·73	100
Nitrate of strontia	6·79	100·89

13. *Nitrate of lime.*—Time of diffusion 11·43 days. The diffusate was evaporated to dryness with an excess of sulphuric acid, and the nitrate of lime, which is always supposed anhydrous, was estimated from the sulphate of lime produced.

Diffusion in 11·43 days at 64°·1 ; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·66	1·021
From 2 per cent solution . . .	15·01	2
From 4 per cent solution . . .	29·04	3·372
From 8 per cent solution . . .	55·10	7·334

The results throughout for this salt are almost identical with those of nitrate of baryta, although these two salts differ greatly in solubility, and in one being a hydrated, and the other an anhydrous salt.

14. *Acetate of lead.*—Diffused for 16·166 days ; the time chosen formerly for sulphate of magnesia, with seven days for chloride of sodium. The solution contained 0·965 per cent of anhydrous salt, with the density 1·0080. As this solution of acetate of lead was found to be precipitated by pure water, about 2 per cent of strong acetic acid was introduced into the solution, and the same acid was added in a less proportion to the water jars. The salt of lead diffused was afterwards determined by means of sulphuric acid. Diffused in eight cells, at 53°·1, 7·45, 7·29, 7·46 and 8·07 grs. ; mean 7·56 ; or 7·84 for 1 per cent in two cells.

15. *Acetate of baryta.*—Diffused for 16·166 days. The solution contained 0·977 per cent of anhydrous salt, with the density 1·0073. The same addition of acetic acid was made to it as to the preceding acetate of lead, in order that the circumstances of diffusion might be similar for both salts. The salt diffused was estimated also in the form of sulphate.

Diffusion of 1 per cent solutions in 16·166 days ; two cells.

Acetate of baryta at 53°·5 . .	7·50	100
Acetate of lead at 53°·1 . . .	7·84	104·53

Here, of two isomorphous salts, that of greatest atomic weight sensibly exceeds the other in diffusibility.

16. *Chloride of barium.*—Time of diffusion 11·43 days. The diffused salt was weighed as sulphate of baryta.

Diffusion in 8·57 days at 63°; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·32	1·047
From 2 per cent solution . . .	12·07	2
From 4 per cent solution . . .	23·96	3·970
From 8 per cent solution . . .	45·92	7·608

17. *Chloride of strontium.*—The diffused salt was weighed as sulphate of strontia.

Diffusion in 8·57 days at 63°; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·09	1·045
From 2 per cent solution . . .	11·66	2
From 4 per cent solution . . .	23·56	4·041
From 8 per cent solution . . .	44·46	7·626

The series of ratios in the preceding table will be found, on comparison, to correspond closely with the ratios of chloride of barium. It may be useful to compare farther the amounts diffused from similar solutions of these two isomorphous compounds.

Diffusion in 8·57 days at 63°; two cells.

Chloride of barium, 1 per cent . .	6·32	100
Chloride of strontium, 1 per cent .	6·09	96·36
Chloride of barium, 2 per cent . .	12·07	100
Chloride of strontium, 2 per cent .	11·66	96·90
Chloride of barium, 4 per cent . .	23·96	100
Chloride of strontium, 4 per cent .	23·56	99·16
Chloride of barium, 8 per cent . .	45·92	100
Chloride of strontium, 8 per cent .	44·46	96·83

The near coincidence of the 4 per cent solutions probably arises from an accidental error of observation in the chloride of barium, for the latter departs here from the progression of its ratios. We appear then to have a small but constant difference of about 3½ per cent in the diffusion of these two isomorphous salts, the chloride of barium, which possesses the highest atomic weight, having the advantage.

The diffusion of the 1 per cent solution of the same salts for the longer period of 11·43 days, gives 7·50 for chloride of barium at 50°·9, and 7°·52 for chloride of strontium at 51°, or nearly the same temperature. For the first time we have in the barytic salts a divergence between chlorides and nitrates, for the nitrates of the same bases have a number about 6·8 only at the same temperature. I am led, however, to believe that this discrepancy becomes much

less at low temperatures by experiments which are at present in progress.

18. *Chloride of calcium.*—Time of diffusion 11·43 days. The salt diffused was weighed as sulphate of lime.

Diffusion in 11·43 days at 63°·8; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·92	1·032
From 2 per cent solution . . .	15·35	2
From 4 per cent solution . . .	30·78	4·010
From 8 per cent solution . . .	61·56	8·021

We may now observe how far the diffusion of the chloride of calcium is analogous to that of nitrate of lime. At the inferior temperatures, the results for the 1 per cent solution of these two salts were as follow:

Chloride of calcium at 50°·9 . .	6·51	100
Nitrate of lime at 51°·5 . . .	6·54	100·46

While at the higher temperatures, namely 63°·8 for the chloride of calcium, and 64°·1 for the nitrate of lime, the results for the different proportions of salt are:

Chloride of calcium, 1 per cent . .	7·92	100
Nitrate of lime, 1 per cent . . .	7·66	96·72
Chloride of calcium, 2 per cent . .	15·35	100
Nitrate of lime, 2 per cent . . .	15·01	97·79
Chloride of calcium, 4 per cent . .	30·78	100
Nitrate of lime, 4 per cent . . .	29·04	94·35
Chloride of calcium, 8 per cent . .	61·56	100
Nitrate of lime, 8 per cent . . .	55·10	89·51

The correspondence between the 1 and 2 per cent solutions of chloride and nitrate is sufficiently close, but in the 4 and 8 per cent the salts diverge, as happens also with hydrochloric and nitric acids themselves. The nitrate in both falls off, while the chloride sustains throughout the high diffusibility of the lower proportions.

19. *Chloride of manganese.*—Time of diffusion 11·43 days. The salt diffused was estimated by means of nitrate of silver.

The 1 per cent solution, of density 1·0085, gave at 50°.8, in eight cells, 6·67, 6·26, 6·79 and 6·81 grs.; mean 6·63 for two cells.

20. *Nitrate of magnesia.*—Time of diffusion 11·43 days. The salt diffused was estimated as sulphate.

The 1 per cent solution, of density 1·0073, gave at 50°·8, in eight cells, 6·29, 6·39, 6·52 and 6·76 grs.; mean 6·49 for two cells.

21. *Nitrate of copper.*—Time of diffusion 11·43 days. The salt diffused was estimated from the oxide of copper obtained by ignition.

The 1 per cent solution, of density 1·0075, in eight cells, at 50°·8, gave 6·52, 6·36, 6·18 and 6·70 grs.; mean 6·44 for two cells.

Comparing the preceding salts with chloride of calcium diffused at the same temperature, 50°·8, we have the following results:

Chloride of calcium	6·51	100
Chloride of manganese . . .	6·63	101·15
Nitrate of magnesia	6·49	99·69
Nitrate of copper	6·44	98·92

This group of salts, belonging to the same isomorphous family of bases, the magnesian, again corresponds closely in diffusibility.

The following additional magnesian chlorides were diffused, all 1 per cent solutions, either in six or in eight cells. The salt diffused was estimated by means of nitrate of silver.

The results referred to chloride of calcium, at nearly the same temperature, 50°·8, are as follow:

Chloride of calcium	6·51	100
Chloride of zinc	6·29	96·61
Chloride of magnesium . . .	6·17	94·77
Chloride of copper	6·06	93·08

These salts present a greater latitude in their diffusibility, if belonging to the same class, than is usual.

22. *Protochloride of iron.*—A solution of this salt of 1·023 per cent was diffused at 53°·5, a somewhat higher temperature than the corresponding chlorides. It gave 6·45, 6·48, 6·48 and 6·28 grs. in two cells; mean 6·44, or 6·30 for 1 per cent in two cells. This salt appears therefore to belong to the last group.

23. *Sesquichloride of iron.*—A full series of observations was made upon the diffusion of the different proportions of this salt from 1 to 8 per cent, but in all of them decomposition was determined by the diffusion, with turbidity also in the solution-phial, except in the 8 per cent solution.

The mean diffusion from the 1 per cent solution in 11·43 days, at 63°·3, was 4·13 grs. of sesquichloride of iron with 1·28 gr. of free hydrochloric acid, in two cells. This result indicates that one-half nearly of the sesquichloride of iron is decomposed in the diffusion.

The mean diffusion from the 8 per cent solution, at 63°·3, was 55·88 grs. of sesquichloride of iron, with 6·66 grs. of free hydrochloric acid, in two cells. It appears from this experiment that perchloride of iron approaches the chloride of calcium in diffusibility. That the proto- and persalts of the magnesian metals should have a similar rate of diffusion is not unlikely, from other analogies which they exhibit.

24. *Sulphate of magnesia.*—The time chosen for the diffusion of this salt, namely 16·166 days, is a multiple by 2 of the time of

sulphate of potash, and by 4 of the time of hydrate of potash. The diffusate was evaporated to dryness and weighed.

Diffusion in 16·16 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·31	1·144
From 2 per cent solution . . .	12·79	2
From 4 per cent solution . . .	23·46	3·671
From 8 per cent solution . . .	42·82	6·701
From 8 per cent solution at 62°·8 .	42·66	1
From 16 per cent solution at 62°·8	75·06	1·759
From 24 per cent solution at 62°·8	102·04	2·340

25. *Sulphate of zinc.*—Time of diffusion 16·166 days. The diffused salt was evaporated to dryness and weighed.

Diffusion in 16·16 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·67	1·091
From 2 per cent solution . . .	12·22	2
From 4 per cent solution . . .	23·12	3·784
From 8 per cent solution . . .	42·26	6·916
From 8 per cent solution at 62°·8 .	39·62	1
From 16 per cent solution at 62°.8	74·40	1·878
From 24 per cent solution at 62°·8	101·42	2·560

It will be remarked that the diffusion of these two isomorphous salts, sulphate of magnesia and sulphate of zinc, differs so much in the 1 per cent solution, as 7·31 to 6·67, that is, as 100 to 91·25; or 8·75 per cent. This, I have no doubt, however, is an accidental error, the disturbances from changes of temperature and other causes of dispersion being in direct proportion to the duration of the experiment, and therefore much increased with these long times; while the 1 per cent solution also appears to be generally the proportion most exposed to such errors. The sulphate of zinc appears to be the truest throughout in its diffusion, of these two salts. The approach to equality becomes close in the 4 per cent and larger proportions of salt, particularly with the unusually high proportions of 16 and 24 per cent, which were observed in these salts. The diffusion of both salts falls off remarkably in the higher proportions. The result of the comparison of these two magnesian sulphates is no doubt favourable to the similarity of diffusion of isomorphous salts.

26. *Sulphate of alumina.*—The time of diffusion chosen was 16·166 days, or the same as that for sulphate of magnesia. The usual number of eight cells of the 1 and 2 per cent solutions were diffused, and four cells of the 4 and 8 per cent solutions. The whole diffusates of each proportion were then mixed together and the quan-

tities of alumina and sulphuric acid, diffused for two cells, determined separately.

Diffusion in 16·166 days at 65°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	5·48	1·074
From 2 per cent solution . . .	10·21	2
From 4 per cent solution . . .	19·28	3·780
From 8 per cent solution . . .	33·52	6·572

The diffusion of sulphate of alumina, it will be observed, is very sensibly less than that of sulphate of zinc at the same temperature.

27. *Nitrate of silver.*—Time of diffusion seven days. The quantity of salt diffused was ascertained by precipitation with hydrochloric acid, and weighing the chloride of silver formed.

Diffusion for seven days at 63°·4; two cells.

	Grs.	Ratio.
From 2 per cent solution . . .	13·61	2
From 4 per cent solution . . .	26·34	3·87
From 8 per cent solution . . .	51·88	7·62

28. *Nitrate of soda.*—Time of diffusion seven days. The quantity of salt diffused was ascertained by evaporation to dryness.

Diffusion in seven days at 63°·4; two cells.

	Grs.	Ratio.
From solution of 2 per cent . .	12·35	2
From solution of 4 per cent . .	23·56	3·82
From solution of 8 per cent . .	47·74	7·72

The ratios of the last column of the preceding Table are sensibly the same as those already obtained for nitrate of silver. But the diffusibility of nitrate of soda appears to be increased less rapidly by temperature than nitrate of silver. Hence the diffusibility of these two salts appears more similar at low than high temperatures.

Diffusion from 2 per cent solutions in seven days at 53°.

Nitrate of silver	11·24	100
Nitrate of soda	10·81	96·17

Diffusion from 2 per cent solutions in seven days at 63°·4.

Nitrate of silver	13·61	100
Nitrate of soda	12·35	90·74

29. *Chloride of sodium.*—Time of diffusion seven days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

Diffusion in seven days at 63°·4; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·32	1·023
From 2 per cent solution . . .	12·37	2
From 4 per cent solution . . .	24·96	4·036
From 8 per cent solution . . .	48·44	7·832

These numbers resemble closely those obtained in the diffusion of chloride of barium during the longer period of 8·57 days.

The chloride of sodium and nitrate of soda will be seen to exhibit the usual approach to parallelism between the chloride and nitrate of the same metal, by the following comparison:

Diffusion of both at 63°·4.

Chloride of sodium, 2 per cent . .	12·37	100
Nitrate of soda, 2 per cent	12·35	99·83
Chloride of sodium, 4 per cent . .	24·96	100
Nitrate of soda, 4 per cent	23·58	94·48
Chloride of sodium, 8 per cent . .	48·44	100
Nitrate of soda, 8 per cent	47·74	98·55

As usual, the chloride is slightly more rapid in its diffusion than the nitrate.

30. *Chloride of potassium.*—Time of diffusion 5·71 days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

Diffusion in 5·71 days at 62°; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6·69	1·005
From 2 per cent solution . . .	13·32	2
From 4 per cent solution . . .	25·94	3·895
From 8 per cent solution . . .	53·64	8·054

The ratios are in remarkably close accordance with the proportions of salt diffused.

The times 5·71 and seven days chosen for the chlorides of potassium and sodium, it will be observed, are as the square roots of 2 and 3. A certain deviation from this ratio of the times of equal diffusion, appears on comparing the experimental results obtained at present for these salts.

Diffusion of chloride of potassium in 5·71 days at 62°, and of chloride of sodium in 7 days at 63°·4.

Chloride of potassium, 1 per cent . .	6·69	100
Chloride of sodium, 1 per cent . . .	6·32	94·47
Chloride of potassium, 2 per cent . .	13·32	100

Chloride of sodium, 2 per cent . . .	12·37	92·86
Chloride of potassium, 4 per cent . .	25·94	100
Chloride of sodium, 4 per cent . . .	24·96	96·23
Chloride of potassium, 8 per cent . .	53·64	100
Chloride of sodium, 8 per cent . . .	48·44	90·30

The difference would be about 1 per cent greater if the diffusion of both salts were reduced to the same temperature. The chloride of potassium deviates of course from the nitrate of soda in a similar manner. But chloride of potassium corresponds more closely with nitrate of silver than with chloride of sodium and nitrate of soda, at the temperature of the experiments.

Diffusion of chloride of potassium for 5·71 days at 62°, and of nitrate of silver for 7 days at 63°·4.

Chloride of potassium, 2 per cent . .	13·32	100
Nitrate of silver, 2 per cent	13·61	102·18
Chloride of potassium, 4 per cent . .	25·94	100
Nitrate of silver, 4 per cent	26·34	101·54
Chloride of potassium, 8 per cent . .	53·64	100
Nitrate of silver, 8 per cent	51·88	96·71

The coincidence in rate would appear even closer in the 2 and 4 per cent solutions, if the diffusion of the nitrate of silver was diminished about 1 per cent, on account of its higher temperature. It might thus be supposed that the nitrate of silver followed the sodium rate more accurately than the nitrate of soda and chloride of sodium themselves do.

A series of observations were made upon the diffusion of the 1 per cent solution of chloride of potassium at a nearly constant temperature of 56°, but for different times, varying from five days to eight days, and eighteen hours, to discover the progression, which proved to be pretty similar to that of the 2 per cent solution of hydrochloric acid. Six cells were diffused for each period, of which the mean result is given: the times advance by ten hours.

Diffusion of 1 per cent solution; two cells.

Time.	Temperature.	Diffusion in two cells.	Differences.
5 days	55°·71	5·89	
5 days 10 hours	55 ·90	6·25	0·36
5 days 20 hours	55 ·79	6·55	0·30
6 days 6 hours	55 ·79	6·71	0·16
6 days 16 hours	55 ·90	6·95	0·24
7 days 2 hours	55 ·9	7·48	0·53
7 days 12 hours	55 ·9	7·58	0·10
7 days 22 hours	56 03	8·08	0·50
8 days 8 hours	56 ·28	8·34	0·26
8 days 18 hours	56 ·15	8·60	0·26

When the quantities of chloride of potassium are placed beside the same quantities of hydrochloric acid in the former table, it is found that the times of diffusion of the salt and acid exhibit an approximately constant ratio. The squares of these times of equal diffusion are as 1 to 2·04 for the shortest period of the chloride of potassium, and as 1 to 2·10 for the longest period but one. The variation in the differences towards the middle of the table is too great to be explained, except I fear by some error of observation, although no ordinary precaution was neglected in the execution of this laborious series of experiments.

31. *Iodides and bromides of potassium and sodium.*

Iodide of potassium.—Time of diffusion, 5·716 days. The diffusate was estimated by means of nitrate of silver.

(1). Iodide of potassium, 1·977 per cent; density 1·0145. Diffused at 53°·5, in eight cells, 11·415, 11·506, 10·942 and 11·062 grs.; mean 11·24 for two cells, and 11·36 for 2 per cent.

Comparing this salt with the isomorphous chloride of potassium, we have:

Diffusion of 2 per cent solutions in 5·716 days

Chloride of potassium at 55° . .	11·48	100
Iodide of potassium at 53°·5 . .	11·36	99·65

The diffusion of the iodide would slightly exceed that of the chloride, instead of falling below it as in the table, if the temperatures were made equal.

(2). Again, iodide of potassium 1·971 per cent; observed density 1·01486. Diffused at 59°·8, in eight cells, and the mean diffusate of the whole cells determined, it gave 12·33 grs. of iodide of potassium for two cells; or 12·51 grs. for a 2 per cent solution.

Bromide of potassium.—Time of diffusion and mode of estimating diffusate as above. The solution contained 1·975 per cent of salt, and had a density of 1·014850. Diffused at 59°·8, in eight cells, it gave a mean diffusate of 12·30 grs. for two cells; or 12·46 grs. for 2 per cent.

For comparison, a solution of *chloride of potassium*, containing exactly 2 per cent of salt and having the density 1·0133, was diffused in the same circumstances of time and temperature as the two preceding salts. The mean diffusate of eight cells was 12·24 grs. for two cells.

Hence the following result of the diffusion of three isomorphous salts:

Diffusion of 2 per cent solutions in 5·716 days, at 59°·8.

	Grs.	Ratio.
Chloride of potassium . . .	12·24	100
Bromide of potassium . . .	12·46	101·80
Iodide of potassium	12·51	102·21
Mean	12·40	

Iodide of sodium.—Time of diffusion seven days, temperature 59°·8. A solution of 2·011 per cent and density 1·01618, diffused in eight cells, gave a mean diffusate of 12·24 grs. for two cells; that is, 12·18 grs. for 2 per cent solution.

Bromide of sodium.—Time of diffusion and temperature as above. A solution of 2·146 per cent, of density 1·01726, diffused in eight cells, gave a mean diffusate of 12·80 grs.; that is, 11·93 grs. for 2 per cent.

A comparative experiment was made with a solution of *chloride of sodium*, containing 1·917 per cent of salt and of density 1·01376, in eight cells, at 60°. The diffusates for four pairs of cells were 11·65, 11·75, 11·63 and 11·47 grs.; mean 11·63 grs., which gives by proportion 12·14 grs. for a 2 per cent solution. As the present salt differs only 0°·2 Fahr. in diffusion-temperature from the two preceding salts, which is inadequate to produce an assignable difference of diffusion, the three salts may be supposed to be diffused at the same temperature, without sensible error.

Diffusion of 2 per cent solutions for seven days.

	Grs.	Ratio.
Chloride of sodium at 60° . .	12·14	100
Bromide of sodium at 59°·8 .	11·93	98·27
Iodide of sodium at 59°·8 . .	12·18	100·33
Mean	12·08	

In both these isomorphous groups of salts of potassium and sodium, there is certainly a near approach to equality of diffusion. The times for the salts of the two bases being in the empirical proportion of the square roots of 2 and 3, the mean diffusates also approach pretty closely; namely, 12·40 grs. for the salts of potassium and 12·08 grs. for the salts of sodium, which are as 100 to 97·42 Here the members of each group are certainly very similar to each other in density and probably other physical properties, which was not the case with the equidiffusive group containing the hydrogen acids of the same salt-radicals.

32. *Chloride of ammonium.*—Time of diffusion 5·716 days. The salt diffused was estimated by means of nitrate of silver.

Solution 0·988 per cent; density 1·0036. Diffused at 53°, in

eight cells, 6·09, 6·07, 5·67, 5·87; mean 5·92 grs., and 5·99 for 1 per cent in two cells. This is somewhat more than 5·68, one-half of the diffusate of the 2 per cent solution of iodide of potassium, at nearly the same temperature. The diffusion, however, of the small proportions of salts of ammonium, such as the 1 per cent solution, is apt to be given in excess, from their low density.

33. *Dichloride of copper.*—Time of diffusion seven days, or that of chloride of sodium. The salt diffused was obtained by evaporation to dryness, in an air-bath, after treating the liquid with an excess of chlorine, in the form of chloride, from which the dichloride was calculated.

It was an object of interest to discover whether the dichloride of copper (Cu_2Cl), which should be isomorphous with the chloride of sodium, may separate from the protochloride of copper and other magnesian salts, and assume the high diffusibility of the salts of alkaline metals. But the salt in question is entirely insoluble in water. A solution, however, was obtained by dissolving an equivalent quantity of the red suboxide of copper recently precipitated, in hydrochloric acid, of density 1·033, so as to give one grain of dichloride in every hundred water-grain measures of the solution. This acid solution did not precipitate by dilution with water. The salt was diffused into pure water at a mean temperature of 53°·2.

1. Dichloride of copper diffused, 6·66, 6·57, 7·01 and 6·48 grs.; mean 6·68 grs. in two cells. Chloride of sodium at 53°·4, nearly the same temperature, gave 5·90 grs. in the same time. Reducing the result to the temperature of 51° by an approximative correction, we should have 6·48 grs. of dichloride of copper for that temperature, at which chloride of calcium gave 6·51 grs. in 11·43 days, and protochloride of copper (Cu Cl) 6·06 grs. at nearly the same temperature, also in 11·43 days.

So far as we can judge from an experiment at a single temperature, it would appear that the diffusion of dichloride of copper is more rapid than that of the chloride (Cu Cl), in a proportion which supposes the former compound to possess half the "solution-density" of the latter, the times of equal diffusion 7 and 11·43 days, being when squared as 1 to 2.

With the view of discovering whether the large proportion of hydrochloric acid, amounting to 7 per cent, present in the preceding solution of dichloride of copper, modified the diffusion of the salt, a portion of the same acid solution was treated with chlorine-gas, to convert the copper-salt into chloride, and diffused into water, after the excess of chlorine was removed by agitation of the solution with air. The proportion of salt present was thus increased in weight from 1 to 1·36 per cent. The time of diffusion was 11·43 days, and the temperature 53°.

2. Chloride of copper diffused from a 1·36 per cent solution of the

salt in hydrochloric acid, 5·83, 5·66, and 5·30 grs. in two cells; mean 5·60 grs.

The corresponding diffusion from a 1 per cent solution may be supposed to be less than 5·6 grs., in the proportion of 1·36 to 1, without any great error. The results thus become chloride of copper diffused, 3·98, 3·85 and 3·58 grs.; mean 3·80 grs. in two cells.

It hence appears that the diffusion of chloride of copper is much diminished by the presence of a great excess of hydrochloric acid in the same solution. Different causes suggest themselves for this result, such as the possibility of a combination existing of chloride of copper with chloride of hydrogen, in the acid solution; or the influence which must be admitted of the more soluble substance, in a mixture of two similar substances, in repressing the diffusion of the less soluble. The present result, however, is entirely opposed to the idea that the high diffusibility of the dichloride of copper, observed before is due to the hydrochloride acid present.

3. The diffusion of chloride of sodium also appears to be repressed by contact with a large excess of hydrochloric acid. One per cent of chloride of sodium raised the density of dilute hydrochloric acid from 1·035 to 1·0408. Diffused into pure water for seven days at 52°·9, in eight cells, the diffusates of chloride of sodium were 3·80, 3·87, 4·00 and 3·86 grs.; mean 3·88 for two cells. The diffusion of chloride of sodium is thus reduced in a corresponding measure with that of chloride of copper by association with seven times its weight of hydrochloric acid.

These results are interesting in a very different point of view. I have always watched for the appearance of some absorbent or imbibing power on the part of the acids, more analogous to an endosmotic attraction for water, as usually conceived. If such an attraction existed, it would complicate the phenomena of diffusion, for the volume of water absorbed by the acid would displace and project a portion of the latter into the reservoir, the phial not being extensible. The high diffusibility of hydrochloric and nitric acids would be thus explained. But by such a mechanical displacement, the chloride of sodium would be thrown out in the preceding experiment, as well as the hydrochloric acid, which is not the case.

4. Even in hydrochloric acid, of density 1·124 (25 per cent), the diffusion of 1 per cent of chloride of sodium for seven days, at 56°·6, was found to amount to 4·7 grs. only in two cells, and is less than from a solution in pure water.

5. In comparing the influence of nitric acid with that of hydrochloric acid upon the diffusion of chloride of sodium, it was found that in a 7 per cent solution of nitric acid, the chloride of sodium (1 per cent) was entirely decomposed in the diffusive process, at 56°·6, and gave hydrochloric acid in the full diffusive equivalent of that acid, together with nitrate of soda.

34. *Bicarbonate of potash.*—Time of diffusion 8·083 days, or double that of hydrate of potash. The water of the jars was partially charged with carbonic acid gas, to prevent the decomposition of this and the other bicarbonates in the act of diffusion. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of potash diffused for two cells, converted into the chloride of potassium, evaporated to dryness and weighed.

Diffusion in 8·08 days at 68°·2; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·23	1·029
From 2 per cent solution . . .	14·05	2
From 4 per cent solution . . .	26·72	3·806
From 8 per cent solution . . .	52·01	7·408

35. *Bicarbonate of ammonia.*—Time of diffusion 8·083 days. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of ammonia, diffused for two cells, determined by an alkalimetrical experiment, which was always repeated twice.

Diffusion in 8·08 days at 68°·2; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	6 91	1·013
From 2 per cent solution . . .	13·65	2
From 4 per cent solution . . .	27·00	3·959
From 8 per cent solution . . .	50·10	7·346

The amount and progression of the diffusion of this salt correspond well, for all the proportions diffused, with the preceding isomorphous bicarbonate of potash.

36. *Bicarbonate of soda.*—Time of diffusion 9·875 days. The whole diffusates of each proportion were mixed together, and the quantity of bicarbonate of soda, diffused for two cells, converted into chloride of sodium, evaporated to dryness and weighed.

Diffusion in 9·87 days at 68°·1; two cells.

	Grs.	Ratio.
From 1 per cent solution . . .	7·31	1·059
From 2 per cent solution . . .	13·81	2
From 4 per cent solution . . .	26·70	3·869
From 8 per cent solution . . .	52·38	7·590

A remarkable approach to equality in the diffusion of the bicarbonates of potash and soda, in the times chosen, is observed equally in all the proportions of salt from 1 to 8 per cent.

The results for the three bicarbonates may be stated as follow,

the diffusate of the 2 per cent solution of bicarbonate of potash being made equal to 200, as a standard of comparison.

Diffusion of bicarbonates of potash and ammonia in 8·08 days, at 68°·2, and of bicarbonate of soda in 9·875 days, at 68°·1:

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent solution .	102·9	98·3	104·0
From 2 per cent solution .	200·0	194·3	196·4
From 4 per cent solution .	380·6	384·3	380·0
From 3 per cent solution .	740·8	712·6	748·3

Or, making the diffusate from each proportion of the bicarbonate of potash equal to 100:

	Bicarbonate of potash.	Bicarbonate of ammonia.	Bicarbonate of soda.
From 1 per cent solution .	100	95·53	101·07
From 2 per cent solution .	100	97·15	98·20
From 4 per cent solution .	100	100·97	99·84
From 8 per cent solution .	100	96·19	101·03

The bicarbonate of ammonia is slightly lower in general than the bicarbonate of potash, possibly from a small loss of the former salt by evaporation in the different operations. The times chosen for these two bicarbonates is to that of the bicarbonate of soda, as the square root of 2 to the square root of 3, and the remarkable agreement observed in the diffusion of these salts gives support, therefore, to that relation. In alluding to this relation, however, it is proper to add that the carbonates of potash and soda deviate from it in a sensible degree, and the hydrates of potash and soda very considerably. If the relation, therefore, has a real foundation, it must be masked in the salts last named by differences existing between them in certain properties, the discovery and investigation of which is of the last importance for the theory of liquid diffusion.

37. *Hydrochlorate of morphine.*—Time of diffusion 11·43 days. The crystallised salt was assumed to be of the composition $C_{34}H_{18}NO_6 . HCl + 6HO$, with the equivalent 374·5. The quantity diffused was determined from the chlorine, which was precipitated as chloride of silver in an acid solution. Hydrochlorate of morphine, 1·88 per cent of the salt supposed anhydrous, diffused at 64°·1, in six cells, 11·03, 10·72, 11·01; mean 10·92 grs. of the anhydrous salt for two cells. Calculated for 2 per cent, 11·60 grs. at 64°·1 for two cells.

38. *Hydrochlorate of strychnine.*—Time of diffusion 11·43 days. The crystallised salt was assumed to be of the composition $C_{42}H_{22}N_2O_4 . HCl + 3HO$, with the equivalent 397·5. Hydrochlo-

rate of strychnine, 2 per cent, density 1·0065, diffused at 64°·1, in six cells, 11·54, 11·62, 11·31; mean 11·49 grs. for two cells. The quantities refer to anhydrous salt, and were estimated from the chlorine, as with hydrochlorate of morphine.

These two analogous salts appear to approach very closely in diffusibility.

Diffusion from 2 per cent solutions at 64°·1; two cells.

Hydrochlorate of morphine . .	11·60	100
Hydrochlorate of strychnine . .	11·49	99·05

For a similar period of 11·43 days, but at a lower temperature, 53°·4, the 1 per cent solution of hydrochlorate of morphine gave a mean result of 5·49 grs. from two cells and the hydrochlorate of strychnine 5·77 grs. from two cells. But the weights of chloride of silver from which these numbers are deduced were too small to admit of much precision.

The diffusion of these salts of organic bases in 11·43 days, is exceeded by the diffusion of chloride of ammonium or potassium in 5·71 days, or half the former time. The vegeto-alkalies appear thus to be divided from ammonia and potash.

The new observations of the present paper are favourable to the existence of a relation amounting to close similarity or equality in diffusibility between certain classes of substances.

The chlorides and nitrates of the same metal generally exhibit this correspondence, as in the chloride of calcium and nitrate of lime, the chloride of sodium and nitrate of soda, and also in hydrochloric and nitric acids.

Isomorphous salts exhibit the same relation, as has been observed in the chlorides, bromides and iodides of potassium, sodium and hydrogen, in various salts of baryta, strontia and lead, in numerous magnesian salts, in the salts of silver, soda, and probably those of suboxide of copper, and in several additional salts of potash and ammonia.

Corresponding salts of two of the vegeto-alkalies are also found to be equidiffusive.

Before discussing the relations between the different groups of equidiffusive substances which are thus formed, it will be necessary to examine their diffusion at widely different temperatures, a subject attended with considerable difficulty.

Theory of Etherification.

By A. W. Williamson, Ph.D.*

When sulphuric acid is brought in contact with alcohol under certain circumstances, a new arrangement is effected in the elements of the alcohol, which divide into two groups, forming ether and water. Now it is well known that the process by which this change is effected may be represented in two ways, the difference of which consists in their respectively selecting for starting-point a different view of the constitution of alcohol. According to the one view, an atom of alcohol weighs 23, and is made up of $C^2 H^6 O$; so that to form ether, two atoms of it are needed, one of which takes $C^2 H^4$ from the other, setting free the water with which these elements were combined; whereas, according to the other view, alcohol weighs 46, and *contains* ether and water. These are not the only points of difference which are urged; but they are the most real and tangible, and their consideration is sufficient for our present purpose. If by any direct fact we could decide which of these two expressions is the correct one, the ground would be clear for an examination of the process of etherification itself.

The following experiments were made with the view of obtaining new alcohols, by substituting carburetted hydrogen for hydrogen in a known alcohol. With this view an expedient was adopted, which may render valuable services on similar occasions. It consisted in replacing the hydrogen first by potassium, and acting upon the compound thus formed by the chloride or iodide of the carburetted hydrogen which was to be introduced in the place of that hydrogen. The process was first tried with common alcohol, which, after careful purification, was saturated with potassium, and as soon as the action had ceased, mixed with a portion of iodide of ethyl equivalent to the potassium used. Iodide of potassium was readily formed on the application of a gentle heat, and the desired substitution was effected; but, contrary to expectation, the compound thus formed had none of the properties of an alcohol—it was nothing else than common ether, $C^4 H^{10} O$.

Now this result at once appeared to be inconsistent with the higher formula of alcohol; for if that body contained twice as many atoms of oxygen as are in ether, the product ought clearly to have contained twice as much oxygen as ether does. The alternative was evident; for having obtained ether by substituting $C^2 H^5$ for H in alcohol, the relative composition of the two bodies is represented *by expressing that fact in our formula.* Thus alcohol is $\begin{matrix} C^2 H^5 \\ H \end{matrix} O$,

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and the potassium compound is $\begin{matrix} C^2\,H^5 \\ K \end{matrix}\,O$; and by acting upon this by iodide of ethyl, we have

$$\begin{matrix} C^2\,H^5 \\ K \end{matrix}\,O + C^2\,H^5\,I = IK + \begin{matrix} C^2\,H^5 \\ C^2\,H^5 \end{matrix}\,O.$$

Of course, the proportion between the two bodies is the only point here considered, and the same reasoning would be applicable to any multiple of the formulæ assumed. Some chemists may perhaps prefer doubling them, in order to avoid the use of atoms of hydrogen, potassium, &c.; but the author has not felt himself justified in doing so, because that would involve doubling the usual formula for water; for, as will be presently shown, water is formed in etherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen, thus:

$$\begin{matrix} H \\ H \end{matrix}\,O, \quad \begin{matrix} C^2\,H^5 \\ H \end{matrix}\,O, \quad \begin{matrix} C^2\,H^5 \\ C^2\,H^5 \end{matrix}\,O.$$

This formation of ether might, however, be explained, after a fashion, by the other theory—by supposing the potassium compound to contain ether and potash, which separate during the action of the iodide of ethyl; so that half the ether obtained would have been contained in that compound, and the other half formed by double decomposition between potash and iodide of ethyl, thus:

$$\begin{matrix} C^4\,H^{10}\,O \\ K^2\,O \end{matrix} + C^4\,H^{10}\,I^2 = 2\,IK + 2\,(C^4\,H^{10}\,O).$$

But although the insufficiency of this explanation becomes evident on a little reflection, a further and more tangible method of arriving at a conclusion was devised. It consisted in acting upon the potassium compound by iodide of methyl, in which case, if that compound were ether and potash, the resulting mixture should consist of ether and oxide of methyl; whereas, in the contrary case, a body of the composition $C^3\,H^8\,O$ should be formed. Now this substance was actually obtained, and neither ether nor oxide of methyl.

In this experiment, the two theories cross one another, and must lead to different results; for it is evident that, in the first-mentioned decomposition by which ether was formed, the only difficulty in explaining the process decisively, consisted in our inability to prove that the carburetted hydrogen introduced instead of the hydrogen did not have in the product an atom of oxygen to itself, but that, on the contrary, it was coupled with the carburetted hydrogen already contained in the alcohol—the two in combination with one

atom of oxygen. It is clear that if alcohol *contains* ether and water, and the carburetted hydrogen in the first experiment formed a second atom of ether by taking the place of the hydrogen of this water, the process being the same in the second experiment, we should then have obtained two ethers; whereas, if the formation of ether from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate ether which was really produced.

The boiling-point of this remarkable body, is a little above 10° C.; it has a very peculiar smell, distinctly different from that of common ether; and, like that body, it is only slightly soluble in water. It is not acted upon by the alkali-metals at the common atmospheric temperature.

By acting upon the potassium-alcohol in like manner by iodide of amyl, a similar substitution was effected of the elements of that carburetted hydrogen in the place of the hydrogen of alcohol, and an ether obtained which boiled at 111° C., and had the composition $C^7 H^{16} O$. There is some reason to believe that this body is the same which Balard obtained by decomposition of chloride of amyl by an alcoholic solution of hydrated potash, and which that distinguished chemist took for oxide of amyl.

From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be effected in the others; and this expectation has been verified by experiment. Of course, the formulæ of the other alcohols must be reduced to half, for the same reasons as that of common alcohol. Methylic alcohol is, therefore, expressed by the formula $\begin{matrix} C\,H^3 \\ H \end{matrix} O$, as common alcohol is $\begin{matrix} C^2\,H^5 \\ H \end{matrix} O$; and in the same manner amylic alcohol is $\begin{matrix} C^5\,H^{11} \\ H \end{matrix} O$, and the same of the higher ones. In conformity to this fact, we must be able to obtain the same intermediate ethers by replacing hydrogen in these alcohols (methylic and amylic) by the carburetted hydrogen of iodide of ethyl, as by the inverse process described above. This has been verified in the case of the three-carbon ether, which may be obtained indifferently by replacing one-fourth of the hydrogen of methylic alcohol by $C^2 H^5$, or by replacing one-sixth of the hydrogen of common alcohol by CH^3. Its rational formula is, therefore, $\begin{matrix} C^2\,H^5 \\ C\,H^3 \end{matrix} O$.

By acting upon the compound $\begin{matrix} C\,H^3 \\ K \end{matrix} O$ by iodide of amyl, a third ethereal compound was obtained, of which the formula is $\begin{matrix} C\,H^3 \\ C^5\,H^{11} \end{matrix} O$. This is evidently the only one of the three new ethers, which, containing an even number of carbon atoms, might be conceived to have

been formed from one alcohol; but when treated with monobasic acids, as the hydrochloric, it cannot be expected to act in the same manner as its homogeneous isomeric, the ether $\begin{matrix} C^3\ H^7 \\ C^3\ H^7 \end{matrix}$ O of the three-carbon alcohol $\begin{matrix} C^3\ H^7 \\ H \end{matrix}$ O.

The next thing to be done is to explain the process of etherification by the action of sulphuric acid ($SO^4\ H^2$) upon alcohol; and in order to accomplish that, we must show the connexion between those substances and the reagents used in the above-described experiments. With this view, we have merely to add to the above facts, the acknowledged analogy of the simple and compound radicals in their compounds. It must first be shown how a substance analogous to the iodide of ethyl is formed, and then how by double decomposition with alcohol it produces ether. This is very easy; for sulphovinic acid is strictly analogous to iodide of ethyl plus iodide of hydrogen, which we should obtain by replacing SO^4 in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of ether, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter; thus:

$$\frac{\begin{matrix} H \\ H \end{matrix}\ SO^4}{\begin{matrix} C^2\ H^5 \\ H \end{matrix}\ O} = \frac{\begin{matrix} H \\ C^2\ H^5 \end{matrix}\ SO^4}{\begin{matrix} H \\ H \end{matrix}\ O}.$$

Now from this point it is clear that the process is the same as in the decompositions above described; for by this sulphovinic acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming of course sulphuric acid and ether:

$$\frac{\begin{matrix} H \\ C^2\ H^5 \end{matrix}\ SO^4}{\begin{matrix} H \\ C^2\ H^5 \end{matrix}\ O} = \frac{\begin{matrix} H \\ H \end{matrix}\ SO^4}{\begin{matrix} C^2\ H^5 \\ C^2\ H^5 \end{matrix}\ O}.$$

The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which re-acts as before; and so the process goes on continuously, as found in practice.

We thus see that the formation of ether from alcohol is neither a process of simple separation, nor one of mere synthesis; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds. This

view of the matter is therefore consistent with the contact theory, inasmuch as it acknowledges the circumstance of contact as a necessary *condition* of the reaction of the molecules upon one another. By reducing the formulæ of the alcohols to one atom of oxygen, it also retains the equality of volumes which the contact theory insists upon between the vapours of these bodies and their ethers, so that ether truly contains the elements of olefiant gas in addition to those of alcohol in one atom. But, on the other hand, it attaches equal importance to all the essential facts of the chemical theory, and rests the explanation of the process as much upon them as upon those of the contact theory; for, one-sixth of the hydrogen in alcohol truly exhibits different reactions from the remaining five, and must therefore be contained in that compound in a different manner from them; and the alternate formation and decomposition of sulphovinic acid is in this, as well as in the chemical theory, the key to explaining the process of etherification.

Innovations in science frequently gain ground *only* by displacing the conceptions which preceded them, and which served more or less directly as their foundation; but, if the view here presented be considered a step in our understanding of the subject, the author begs leave to disclaim for it the title of innovation; for the conclusion here deduced consists in showing the compatibility of views which have hitherto been considered contrary; and the best possible justification of the eminent philosophers who have advocated either one of the two contending theories, is thus afforded by reconciling their arguments with those of their equally illustrious opponents.

Let us now direct our attention to the transfer of homologous molecules in alternately opposite directions, which, as we have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now, in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged; that if hydrogen and amyl can replace one another in a compound, hydrogen and ethyl, which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound; and that the facility of interchange of hydrogen and methyl, which are still more similar, will be still greater. But if this be true, must not the exchange of one molecule for another of *identical* properties be the most easily effected of all? Surely it must, if there be any difference at all; and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among

substances resembling it in other respects. We are thus forced to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition Cl H, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basylous elements, hydrogen and copper, do not limit their change of place to the circle of the atoms with which they were at first combined,—the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid. Thus it is, that at any moment of time in which we examine the mixture, the bases are divided between the acids; and in certain cases, where the difference of properties of the analogous molecules is very great, it is found that the stronger acid and stronger base remain almost entirely together, leaving the weaker ones combined. This is well known in the case of a mixture of sulphuric acid and borax, and is a confirmation of our fundamental assumption, that the greater the difference of properties, the more difficult is the alternate interchange of one molecule for another.

But suppose now, that instead of sulphate of copper, we mixed sulphate of silver with our hydrochloric acid in aqueous solution, and that a similar division of the bases between the acids established itself in the first moment, forming four compounds, $SO^4 H^2$, $SO^4 Ag^2$, ClH, Cl Ag; it is clear, that this last-mentioned compound, being insoluble in water, must, on its formation, separate out and remove from the circle of decompositions which solubility established. But, of course, the three compounds remaining in solution continue the exchange of their component parts, and give rise successively to new portions of chloride of silver, until as much of that compound is precipitated as the liquid contained equivalents of its component parts, a very small quantity remaining in solution and in the circle of decompositions.

Such is the general process of chemical decomposition. Of course a compound is removed as effectually from the circle of decompositions by assuming the gaseous form under the circumstances of the experiment, or even by being a liquid insoluble in the menstruum. This explanation coincides in its second part with that

which was proposed many years ago by Berthollet; but not making use of the atomic hypothesis, upon which the preceding explanation is based, that eminent philosopher went no farther back than the division of the acids between the bases on the mixture of salts, a fact here deduced from the motion of atoms. It is well known, that the general fact upon which Berthollet founded his view is denied by some eminent chemists of the present day; but the instances which they adduce are perhaps only apparent exceptions to the law, and will, on further examination, be found to afford additional confirmation of the truth of the great Savoysien's conception, as already shown in the case of boracic and sulphuric acids.

In using the atomic theory, chemists have added to it of late years an unsafe, and perhaps unwarrantable hypothesis, namely, that the atoms are in a state of rest. This hypothesis the author of the present paper discards, and reasons upon the broader basis of atomic motion.

On the Constitution of Codeine, and its Products of Decomposition. By T. Anderson, M.D.*

The composition of codeine has been variously stated by different chemists. According to Regnault, the formula of anhydrous codeine is $C_{35}\,H_{20}\,NO_5$, and that of the crystallised base $C_{35}\,H_{20}\,NO_5 + 2\,HO$. Gerhardt, however, objects to this formula, because the numbers of equivalents of carbon and oxygen are uneven, and the sum of the equivalents of hydrogen and nitrogen is likewise indivisible by two. From his own analysis, Gerhardt deduces the formula:

$$C_{36}\,H_{21}\,NO_6,$$

and this formula is fully confirmed by the recent researches of Dr. Anderson.

The codeine with which the author's experiments were made was prepared, as usual, from the mother-liquor from which morphia had been precipitated by ammonia. This liquid was evaporated to crystallisation, and the crystals pressed, to separate the hydrochlorate of ammonia, which is more soluble than the hydrochlorate of codeine, these operations being repeated till the greater part of the sal-ammoniac was got rid of. The crystals of hydrochlorate of codeine were then dissolved in boiling water, and the solution treated with caustic potash, whereby the codeine was precipitated as an oil, which afterwards concreted into a solid mass and was partly deposited in crystals as the solution cooled.

Another crop of crystals may be obtained by evaporating the solution, and the mother-liquor, when concentrated to a small bulk, becomes

* Transactions of the Royal Society of Edinburgh.

filled on cooling with long silky needles of morphia, which had been retained in solution by the excess of potash. The crystals of codeine are purified by solution in hydrochloric acid, boiling with animal charcoal and reprecipitation by potash; and the resulting precipitate is finally dissolved in hydrous ether free from alcohol, to separate any morphia that may adhere to it. Anhydrous ether dissolves codeine much less easily; the solution when evaporated yields small crystals of anhydrous codeine. Codeine, crystallised from water or hydrous ether, forms crystals belonging to the right prismatic system, and containing 2 equivalents of water, which are given off at 212°.

Codeine is an extremely powerful base, rapidly restoring the blue colour of reddened litmus, and precipitating the oxides of lead, copper, iron, cobalt, nickel, &c., from their solutions. It is precipitated by potash from its salts, and is generally stated to be insoluble in that alkali; but this is true only of very highly concentrated solutions, as a considerable quantity of strong potash may be added to a saturated solution of codeine in water without producing precipitation, and even when a very large amount of potash is added, a certain quantity of the base is still retained in solution. Codeine is soluble in ammonia, but not more so than in water; 100 parts of a moderately strong solution of ammonia at 60° dissolve 1·40 parts of codeine; and, according to Robiquet, 100 parts of water at 59° dissolve 1·26 parts. Codeine is precipitated from all its solutions by ammonia; it does not, however, fall immediately, but is slowly deposited in small transparent crystals.

SALTS OF CODEINE.

Hydrochlorate.—$C_{36}\,H_{21}\,NO_6\,.\,HCl$. Obtained by saturating hot hydrochloric acid with pure codeine. A concentrated solution becomes nearly solid on cooling; but a more dilute solution yields radiated groups of short needles, which under the microscope are found to be four-sided prisms with dihedral summits. The crystals are soluble in 20 parts of water at 60°, and in less than their weight of boiling water. The salt dried in the air retains 4 equivs. of water; one which goes off at 212°, and the other three at 250°; the salt at the same time losing acid and aquiring an alkaline reaction. The salt is also sometimes deposited from its solution in anhydrous crystals.

Hydriodate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HI$. Obtained by dissolving codeine in hot hydriodic acid, and leaving the solution to cool, whereupon it is deposited in long slender needles which fill the whole liquid, if it has been sufficiently concentrated. Soluble in 60 parts of cold water; more soluble in boiling water. The crystals contain 2 atoms of water.

Sulphate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HO\,.\,SO_3$. Crystallises in radiated groups of long needles, or by spontaneous evaporation in flattened four-sided prisms. Dissolves in 30 parts of cold water; very

soluble in hot water. Neutral to test paper, when pure; but very apt to retain a small quantity of acid, which can only be got rid of by repeated crystallisation. The crystallised salt contains 5 equivalents of water, which are given off at 212°; the formula of the crystallised salt is $C_{36}\,H_{21}\,NO_6\,.\,HO\,.\,SO_3 + 5\,Aq.$

Nitrate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HO\,.\,NO_5$. Formed by slowly adding nitric acid of specific gravity 1·060 to powdered codeine, an excess of acid being carefully avoided. Easily soluble in boiling water, from which it is deposited in small prismatic crystals on cooling. When heated on platinum, it melts, and on cooling concretes into a brown resinous mass; at a higher temperature, it is rapidly decomposed, leaving a bulky coal difficult of incineration.

Phosphate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HO\,.\,2\,HO\,PO_5$. When tribasic phosphoric acid is saturated with powdered codeine, and the solution mixed with strong spirit, this salt is obtained in small scales or short thick prisms, which are readily soluble in water. They contain 3 equivalents of water of crystallisation, which are given off at 212°.

Oxalate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HO\,.\,C_2\,O_3$. Deposited, on cooling its hot saturated solution, in short prisms, or sometimes in scales. Soluble in 30 times its weight of water at 60°, and about half its weight at 212°. The crystals heated to 212° gave off 3 equivalents of water. At 250° the salt turns brown, and at a higher temperature is entirely decomposed.

Hydrosulphocyanate of Codeine.—$C_{36}\,H_{21}\,NO_6\,.\,HC_2\,NS_2$. Deposited in beautiful radiated needles, on mixing the solutions of hydrochlorate of codeine and sulphocyanide of potassium. The crystals contain 1 equivalent of water, which they give off at 212°.

Chloride of Platinum and Codeine.—A moderately concentrated solution of hydrochlorate of codeine, mixed with bichloride of platinum, deposits a pale-yellow pulverulent precipitate; a more dilute solution yields no immediate precipitate, but after a time deposits minute tufts of silky needles. The salt is soluble in water, and on cooling is deposited partly in grains, partly as a powder; not, however, without partial decomposition. By ebullition with excess of chloride of platinum, it is completely decomposed. To obtain it pure, it must be precipitated in the cold, and without excess of chloride of platinum. The formula of the crystallised salt is $C_{36}\,H_{21}\,NO_6\,.\,HCl + PtCl_2 + 4\,HO$. At 212° it gives off 3 equivalents of water, and the remainder is expelled at 250°, the salt at the same time turning brown and being partially decomposed.

Codeine forms many other crystallisable salts, none of which, however, have been completely examined. The chromate forms fine yellow needles. With solution of corrosive sublimate, codeine forms a white precipitate, soluble in boiling water and alcohol, and deposited in stellate groups of crystals on cooling. With chloride of palladium,

a yellow precipitate is obtained, which is decomposed on boiling, and yields metallic palladium. The tartrate and hydrocyanate of codeine are uncrystallisable.

PRODUCTS OF DECOMPOSITION OF CODEINE.

Action of Sulphuric Acid.—Amorphous Codeine.—When codeine is dissolved in moderately strong sulphuric acid, the mixture digested for a while on the sand-bath, and then treated with carbonate of soda, a grey precipitate is obtained, consisting of codeine in an amorphous state. The precipitate must be collected on a filter, washed with water, dissolved in alcohol, and precipitated from the solution by water. It then forms a grey powder, with more or less of a green shade, insoluble in water, readily soluble in alcohol, and precipitated by ether from the alcoholic solution. Fuses at 212° to a black resinous mass. Readily soluble in acids, forming salts which are amorphous, and dry up by evaporation into brown resins. Analysis shows it to be identical in composition with codeine in its ordinary state. The action of sulphuric acid upon codeine is indeed analogous to that which it produces upon quinine, but the resulting amorphous codeine is not so stable a substance as quinoidine. Moreover, the action does not stop at the point at which amorphous codeine is produced; for if it be continued, a deep-green substance is formed containing sulphur, and analogous to the sulphomorphide described by Arppe, and the corresponding sulphonarcotide of Laurent and Gerhardt.

Action of Nitric Acid.—Nitrocodeine—$C_{36}H_{20}NO_4NO_6$. When strong nitric acid is poured upon codeine, and heat applied, violent action takes place, nitrous fumes are abundantly evolved, and the solution acquires a red colour. If the fluid be evaporated over the water-bath, a yellow resinous acid is left, soluble, with a red colour, in ammonia and potash; but when dilute acid is used, a nitro-base is obtained having the composition above given. The best mode of preparing it, is to add finely powdered codeine to nitric acid of specific gravity 1·060, kept at a moderate heat in a flask, small portions of the liquid being taken out every now and then and tested with ammonia, till the precipitate formed on neutralising the acid, no longer increases in quantity. The liquid is then to be saturated with ammonia, and stirred rapidly, whereupon it will become filled with a bulky precipitate of nitrocodeine. The action is very rapid, and great care must be taken not to let it go too far, otherwise the resinous substance above-mentioned will be produced, its formation being indicated by the escape of red fumes; it is best to stop the action before the whole of the codeine is decomposed; but even then it is impossible to avoid the formation of a small quantity of the resinous substance, its

presence being indicated by the dark colour which the liquid assumes on the addition of ammonia. The precipitate formed by ammonia is in the form of minute silvery plates, with a very slight shade of yellow. It is purified by solution in hydrochloric acid, boiling with animal charcoal, and reprecipitating with ammonia, and subsequently crystallised from a solution in alcohol, or in a mixture of alcohol and ether.

Nitrocodeine crystallised from alcohol is deposited in the form of slender silky needles, which have a pale fawn colour, and, on drying, mat together into a silky mass. From alcohol and ether it is obtained by spontaneous evaporation in small yellowish crystals, which, under the microscope, are seen to consist of four-sided prisms terminated by dihedral summits. Nitrocodeine is sparingly soluble in boiling water, from which it is deposited in minute crystals on cooling. It dissolves abundantly in boiling alcohol, but sparingly in ether. It is soluble in acids, forming salts which are neutral to test paper, and yield the base in the form of a crystalline powder on the addition of potash or ammonia. When heated carefully, it melts into a yellow liquid, which concretes on cooling into a highly crystalline mass. At a higher temperature it decomposes suddenly without flame, leaving a bulky charcoal. Crystallised nitrocodeine is anhydrous.

Hydrochlorate of Nitrocodeine is obtained by dissolving nitrocodeine in hydrochloric acid, and evaporating the solution, whereupon the salt is left in the form of a resinous mass, which cannot be made to crystallise.

Sulphate of Nitrocodeine, $C_{36}\,H_{20}\,(NO_4)\,NO_6 . HO . SO_3$, forms radiated groups of short-pointed needles, neutral to test-paper, and very soluble in boiling water.

Oxalate of Nitrocodeine crystallises in short prisms of a fine yellow colour, readily soluble in water.

Platinochloride of Nitrocodeine, $C_{36}\,H_{20}\,(NO_4)\,NO_6 . HCl + PtCl_2 + 4\,HO$, is precipitated from the solution of the hydrochlorate in the form of a yellow powder, insoluble in water and alcohol.

By treating an alcoholic solution of nitrocodeine with hydrosulphate of ammonia, a new base is obtained, which, from its analogy with other compounds similarly prepared, is probably composed of $C_{36}\,H_{22}\,N_2\,O_6$, and may be called *Azocodeine*; it has not yet, however, been completely examined, on account of the great difficulty of preparing and purifying it.

Action of Bromine on Codeine.—Bromocodeine—$C_{36}\,H_{20}\,BrNO_6$. When bromine-water is added in small successive portions to finely powdered codeine, the base is rapidly dissolved, the solution losing its colour of bromine, and acquiring a peculiar and characteristic red shade. After a certain quantity of bromine has been added, small crystals make their appearance, which are hydrobromate of codeine; but these

are only observed if the bromine-water has been thoroughly saturated, and are deposited in a small quantity only, the remainder being retained in solution. When the whole of the codeine has been dissolved, ammonia is added, and bromocodeine is immediately thrown down as a silvery-white powder; in this state it contains a small quantity of unchanged codeine. It is collected on a filter, washed several times with cold water, and redissolved in hydrochloric acid, from which it is precipitated by ammonia, and finally crystallised from boiling spirit. Bromocodeine is scarcely soluble in cold water; but by boiling, a somewhat larger quantity is taken up, and deposited again on cooling in minute prisms terminated by dihedral summits. It is readily soluble in alcohol, particularly on boiling, and is best crystallised from spirit diluted with its own bulk of water. The crystals are always very small, but brilliantly white. It is soluble in ether. When heated, it melts into a colourless liquid, which is destroyed at a temperature somewhat above its melting-point. It dissolves in cold sulphuric acid, and the solution becomes dark-coloured when heated. It is attacked by nitric acid, but much less rapidly than codeine itself. Bromocodeine forms two hydrates, the first containing one, and the second two equivalents of water. Hydrochlorate of bromocodeine forms radiated needles closely resembling those of hydrochlorate of codeine. The hydro-bromate is sparingly soluble in cold water, readily soluble in boiling water, and is deposited from the solution in small prismatic crystals. It contains two equivalents of water, which are not expelled at 212°.

Tribromocodeine.—$C_{36}\,H_{28}\,Br_3\,NO_6$. By continuing the addition of bromine-water beyond the point at which bromocodeine is formed, a further action takes places, and a bright-yellow precipitate makes its appearance, which at first re-dissolves in the liquid, but after a time becomes permanent and goes on gradually increasing, till a very large quantity of bromine has been added, when at length a point is reached at which no further precipitate is produced. If the solution be left till next day, however, bromine again causes a precipitate; and if it be added as long as anything falls, and the solution be again left standing, another precipitate is produced, identical in all respects with that before obtained; and this may be repeated day after day for a very considerable time. The yellow precipitate thus obtained is the hydrobromate of tribromocodeine. It is collected on a filter and washed with water, in which it is very sparingly soluble. When this salt is dissolved in dilute hydrochloric acid, and ammonia added, the tribromocodeine is immediately precipitated as a flocculent powder, which must be washed with water, and purified by solution in alcohol and precipitation by water.

Tribromocodeine, as thus obtained, is a bulky white precipitate, perfectly amorphous, and when dry, more or less grey in its colour. It is insoluble in water and ether, but readily soluble in alcohol.

Hydrochloric acid dissolves it sparingly in the cold, but more readily on boiling; in this process, however, it appears to undergo a partial decomposition, as a small quantity is always left insoluble. Heated on platinum-foil it becomes brown, and is entirely decomposed at its melting-point, leaving a coal difficult of incineration.

In such cases as have been hitherto examined, the substitution of three equivalents of bromine in a base has entirely destroyed its basic properties; but tribromocodeine is a base, though a very feeble one. Its salts are all sparingly soluble in water, and amorphous. The *hydrochlorate* is obtained by dissolving the base in hot dilute hydrochloric acid, and is deposited on cooling as an amorphous powder. The *hydrobromate* is the substance deposited during the preparation of the base. It is a bright-yellow powder, perfectly amorphous, and very sparingly soluble in cold water; on boiling, however, a larger quantity is taken up, and is again deposited on cooling. Its composition appears to be $2\,(C_{36}\,H_{18}\,Br_3\,NO_6)+H\,Br$. The platinochloride is a brownish-yellow powder, soluble in water and alcohol.

The action of bromine on codeine does not terminate with the production of the base just described, but the author has not pursued the investigation any further. There must also exist a *dibromocodeine*, $C_{36}\,H_{19}\,Br_2\,NO_6$, but it has not yet been actually obtained.

Action of Chlorine on Codeine.—Chlorocodeine—$C_{36}\,H_{20}\,Cl\,NO_6$. The action of chlorine on codeine is more complex than that of bromine. When chlorine gas is passed into an aqueous solution of codeine, or chlorine-water added to it, the liquid turns brown, becoming continually deeper in colour, and on the addition of ammonia yields an amorphous resinous base. As there were no means of determining when the action was complete, the product was not further examined. A definite compound, analogous to bromocodeine was, however, obtained by dissolving codeine in excess of dilute hydrochloric acid at about 150° or 160° Fahr., adding finely pounded chlorate of potash—agitating the liquid—continually testing with ammonia, and adopting precautions similar to those required in the preparation of nitrocodeine, and finally precipitating by ammonia. The reaction is as follows:

$$3\,(C_{36}\,H_{21}\,NO_6.\,H\,Cl)+3\,H\,Cl+K\,O.\,Cl\,O_5=K\,Cl+6\,HO+3\,(C_{36}\,H_{20}\,Cl\,NO_6.\,HCl.)$$

The chlorocodeine is precipitated in the form of a silvery crystalline powder, closely resembling bromocodeine. It has generally a yellowish colour, and retains a small portion of codeine, from which it is purified by dissolving in hydrochloric acid, boiling with animal charcoal, and reprecipitating with ammonia. It is finally obtained in crystals from its solution in boiling spirit.

Chlorocodeine is sparingly soluble in boiling water, and the solution

on cooling deposits minute crystals exactly similar to and isomorphous with those of bromocodeine. It is readily soluble in strong alcohol, especially with the aid of heat, and sparingly soluble in ether. It dissolves in sulphuric acid in the cold, without change, but the solution is charred by heating. Nitric acid dissolves it, and the solution is decomposed by boiling, but not by any means so readily as codeine. Red fumes are evolved, together with a peculiar and excessively pungent vapour.

The salts of chlorocodeine are exactly similar to those of bromocodeine. The *hydrochlorate* crystallises in groups of needles, readily soluble in water. The *sulphate*, $C_{36}\,H_{20}\,Cl\,NO_6\,.\,HO\,.\,SO_3 + 4\,Aq$, is deposited from its hot solution in radiated groups of short prisms, which dissolve abundantly in boiling water and alcohol. The *platinochloride* is obtained in the usual way, in the form of a pale-yellow precipitate, scarcely soluble in water.

Action of Cyanogen on Codeine.—Dicyanocodeine—$C_{36}\,H_{21}\,NO_6\,.\,2\,C_2\,N$.—When cyanogen is passed into a solution of codeine in the smallest possible quantity of alcohol, the gas is rapidly absorbed, the liquid acquiring first a yellow, and by continued action, a brown colour. If the solution be then left to itself for some time, the smell of cyanogen disappears and is replaced by that of hydrocyanic acid, and crystals are gradually deposited. If the cyanogen be passed through the solution in a slow continuous current, the deposit of crystals is very abundant. These are collected on a filter, and washed with a small quantity of alcohol; and the filtrate, on being again exposed to the action of cyanogen, yields an additional quantity of crystals, but not so pure as the former. The product is purified by solution, with the aid of heat, in a mixture of alcohol and ether, from which it is deposited in crystals which are colourless or slightly yellow. Obtained in this way, however, they are apt to retain a small quantity of codeine, and it is therefore advantageous to pass cyanogen into the mixture to be used for their solution, by which means the last traces of codeine are converted into the new compound.

Dicyanocodeine is soluble in boiling absolute alcohol or a mixture of alcohol and ether, and is deposited on cooling in anhydrous, thin, six-sided plates, having a brilliant lustre. It is difficultly soluble in water, but is dissolved on the addition of alcohol. Nothing, however, is deposited from the solution on standing, and by evaporation it is decomposed, and crystals of codeine are left behind. With hydrochloric acid it is converted into a crystalline salt, but decomposition take place immediately; for, on the addition of potash to the liquid, ammonia escapes, and, if it be left for twenty-four hours, hydrocyanic acid is evolved. With sulphuric and oxalic acid, dicyanocodeine likewise forms sparingly soluble compounds, which decompose rapidly, with evolution of ammonia and hydrocyanic acid. The instability of these compounds prevented their further examination.

Dicyanocodeine belongs to the same class of compounds as cyaniline, but differs from that substance in containing two equivalents of cyanogen.

ACTION OF ALKALIS ON CODEINE.

Codeine, when treated at moderate temperatures with potash, yields more than one volatile base, according to the circumstances under which the experiment is made. Similar results are obtained by the use of hydrate of potash, or of potash-lime or soda-lime, prepared in the usual way. The method employed in the experiment was to mix codeine with four or five times its weight of potash-lime or soda-lime, and introduce the mixture into a retort with a tubulated receiver, having a doubly bent tube attached to its tubulature, the end of which passed into a small flask containing hydrochloric acid, in order to retain any of the very volatile base which might not be condensed in the receiver. The retort was introduced into an oil-bath, and kept at a uniform temperature of 250° Fahr. As soon as this temperature is reached, a slight peculiar odour is observed, which soon becomes more powerful, and a small quantity of water, retaining the bases in solution, collects in the receiver. The decomposition at 250°, however, is excessively slow, and even after many days, bases are evolved apparently in undiminished quantity; but the mixture was maintained steadily at this point, in hopes of obtaining the product free from ammonia, which the preliminary trials had shown to be produced at higher temperatures; but even with this low heat, it was evolved always in appreciable and, in some experiments, even in considerable quantity. The temperature was, therefore, gradually raised to about 350°, when a larger quantity of base was obtained; and after the heat had been sustained for some time, small crystals made their appearance, which deposited themselves in a line round the retort, just above the level of the oil in the bath, but soon rose into, and collected in the neck of the retort.

These crystals resemble benzoic acid in their external appearance, and are at first perfectly colourless, but soon acquire a brownish shade by exposure to light and air. They are a base, and rapidly restore the colour of reddened litmus. They are sparingly soluble in water, but readily in acids, and give a precipitate with bichloride of platinum. The quantity of this substance obtained was excessively minute; and though considerable quantities of codeine were operated upon, all that was obtained served only to make the few qualitative experiments now detailed.

The watery fluid which collected in the receiver possessed a pungent and peculiar smell; it restored the colour of reddened litmus with great rapidity, and gave abundant fumes with hydrochloric acid. On the addition of solid potash, a highly volatile and pungent oily base

collected as a layer on the surface of the fluid, and at the same time a gaseous base escaped along with ammonia. From the small quantity of these substances obtained, it was impossible to obtain any of them in a pure state. Their constitution was, therefore, determined by the analysis of their platinum-salts, which can be separated from one another, though not without difficulty. In order to prepare these salts, the basic fluid was saturated with hydrochloric acid, and evaporated to dryness in the water-bath, when it left behind a beautifully crystalline mass, highly soluble in water, and deliquescent in moist air. This was dissolved in absolute alcohol, to separate ammonia, and the filtered solution mixed with an alcoholic solution of bichloride of platinum, when the platinum-salts were immediately thrown down as a pale-yellow powder, very sparingly soluble in absolute alcohol, but readily dissolved on the addition of water. The separation of the two bases is best effected by heating the washed precipitate with boiling absolute alcohol, and adding water in small quantities until the whole is dissolved. The crystals which deposit on cooling consist of one of the salts in a state of purity, if the process has been properly managed, or, at all events, only require a repetition of the process to make them absolutely pure. The salt thus obtained is scarcely soluble in absolute alcohol or ether, but is readily soluble in water and dilute spirit, and is thrown down from the latter solution by ether, in the form of fine yellow scales. Its analysis gave results agreeing with the formula $C_2H_5N . HCl . PtCl_2$. The base is, consequently, the methylamine of Wurtz, with whose description of that substance and its platinum-salt it perfectly agrees.

The preparation of the platinum-salt of the other base was attended with much greater difficulty; and it could not be obtained quite free from methylamine. In order to obtain it, the fluid which had deposited the methylamine-salt must be evaporated to a small bulk, the salt which separated filtered off, and ether added to the mother-liquor. Immediately a precipitate is obtained, generally in the form of minute yellow needles, but sometimes in scales. It is sparingly soluble in alcohol and ether, and highly soluble in water, from which it crystallises in long needles, and with such facility that a few drops evaporated on a watch-glass, leave the salt they contain in the form of five or six needles crossing the whole space occupied by the solution. The quantity of this salt was too small to admit of carrying its purification by recrystallisation as far as was to be desired, and consequently a small quantity of methylamine remained in those subjected to analysis.

The results of the analysis approach most closely to the formula $C_6H_9N . HCl . PtCl_2$; consequently that of the base itself C_6H_9N. The base, then, obviously belongs to the same series as methylamine, and forms the term of the series corresponding to metacetonic acid, and, in accordance with the system of nomenclature adopted by Wurtz, it

receives the name of metacetamine. No examination was made of the salts of this base, as it was not obtained in sufficient quantity, but the author takes the opportunity of stating, that before obtaining it from codeine, he had ascertained its existence among the products of destructive distillation of animal substances.*

The residue in the retort after these bases have been evolved, is dark-cinnamon-brown and slightly coherent; it dissolves in water, with a dark-brown, almost black colour, and gives with acids a flocculent brown precipitate of a humus-like substance, and perfectly amorphous, which was not examined. It still contains nitrogen; and by exposure to a heat gradually raised to low redness, it gives an additional quantity of volatile bases, among which ammonia becomes more and more abundant as the temperature rises. A non-basic oil also makes its appearance, but only in very small quantity.

Wertheim† has lately examined the action of soda-lime on certain organic bases. He has obtained metacetamine from narcotine, and methylamine from morphia; and considering these substances to be directly eliminated from the bases, he expects to obtain the residual atoms in the form of a definite compound. Dr. Anderson entertained a similar idea with regard to codeine, until he detected the formation of two different bases, which seemed to him rather to indicate that these substances appear as the result of a true destructive distillation; and that possibly by varying the circumstances of the experiment, other bases may be obtained.

The author has also observed another remarkable decomposition of codeine, by which volatile bases are obtained. The formation by the action of nitric acid, of a resinous acid, has already been mentioned. This acid, which is insoluble in water, dissolves readily in dilute potash, with a red colour; and the solution, on boiling, evolves a volatile base in great abundance. The further examination of the circumstances under which this change takes place, is reserved for a future communication.

Dr. Anderson has likewise examined the action of iodine on codeine, which yields a magnificent crystalline compound, presenting the phenomena of pleochroism in a remarkable manner.

* The author has likewise convinced himself that the petinine described by him two years since as existing in bone-oil, is represented by the formula $C_8 H_{11} N$, and not by $C_2 H_{10} N$, which he then gave for it. He has also ascertained the existence of ethylamine and methylamine in bone-oil.

† Ann. Ch. Pharm. LXXIII, 208.

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IX.—*On the Composition of the Waters of the Dee and Don, at Aberdeen, with an Investigation into the Action of Dee Water on Lead Pipes and Cisterns.*

By John Smith, M.D.

FORDYCE LECTURER ON AGRICULTURE, AND ASSISTANT IN THE LABORATORY OF MARISCHAL COLLEGE.

I.—GENERAL CHARACTER OF THE DISTRICTS DRAINED BY THE RIVERS DEE AND DON.

The sources of the Dee are found amidst the lofty granite mountains of Braemar, on the confines of the counties of Banff, Inverness, and Perth. The river flows from thence, in an easterly direction, along a narrow valley, till it falls into the sea at Aberdeen, its length being about 80 miles, or, when measured in a straight line, 65 miles. The river-banks are gravelly, and the alluvial deposits few, and of limited extent. The bounding ridges of the valley are mostly of granite and gneiss. The flow of the water is pretty rapid, the alteration of level between the Linn (16 or 17 miles below the source) and Aberdeen, being nearly 1200 feet. From the small proportion of clay and peat in the valley of the Dee, its waters are

usually quite clear; in rainy weather, however, they are often charged with mud from the swollen mountain-torrents. The Dee and its tributaries drain about 900 square miles of country.

The rocks near the sources of the Dee are granite and quartzose mica-slate. Though very insoluble in their nature, these rocks will, by slow decomposition, yield to the water minute portions of silica, potash, and iron. The springs of the Dee must, however, be very pure. Further down, the river receives water that flows over patches of crystalline limestone, and a tributary (the Muick) passes along a *serpentine* range. From these rocks, the water will derive a small proportion of lime and magnesia. Proceeding still farther down, the rocks present no variety; granite and gneiss, with occasional veins of felspar-porphyry, and more rarely, patches of limestone, making up the geology of the district.

The water for the supply of Aberdeen is taken from the Dee about two miles from its mouth, and quite beyond the reach of the tide-water. It percolates through the gravelly sides and bottom into drains, and is thence pumped up to the highest level of the town. It is distributed through iron mains, and taken into houses by small lead pipes, to which lead cisterns, generally of moderate dimensions, are commonly attached. The supply is constant, and amounts to about one million gallons per day.

The district drained by the Don lies immediately north of that drained by the Dee, and is of much less extent. Rising in mossy ground, encircled by granite hills, on the borders of Banffshire, the Don pursues a winding course of about 60 miles to Aberdeen. A straight line from its origin to its termination is about 42 miles. The mountainous region drained by the sources of this river, although mainly granitic, has more limestone and serpentine than exist about the Dee, and hence more lime and magnesia might be expected in the water. At Kildrummy, the Don passes through a range of old red sandstone. A few miles below this the hills recede from the river, and enclose the fine valley of Alford. After emerging from the hilly country at Monymusk, its progress is tortuous and slow, through alluvial meadows and an open country, till within a few miles of its termination, when it again flows rapidly. About 18 miles from the sea it receives its largest tributary, the Ury, which drains a fertile country, and has a course of about 24 miles before losing itself in the Don. After rain, the water of the Ury is commonly tinged yellow with clay, while the Don itself has more of a brown colour from peat. The Don water at Aberdeen is rarely of such limpid clearness as that of the Dee.

II.—COMPOSITION OF DEE WATER.

The specimen (*A*) subjected to analysis by the ordinary methods, was collected some miles up the river, on Sept. 24th, 1850, three days after heavy rain. The river was about its usual size, the rain having been preceded by a long-continued drought. The water had a brownish tint from vegetable matter, and, on close inspection, minute specks and hair-like bodies could be observed floating in it. These could be removed by filtration, which, however, did not sensibly improve the colour. The vegetable matter was perceptible to the taste. The water contained little or no air, and I have observed on several other occasions, that when the water is coloured by organic matter, it is deficient in air. The Dee water, in its ordinary condition is colourless, and is well, often highly, aerated. The solid matter found in a gallon of specimen *A* was constituted as follows:

Lime	0·526 grains.
Magnesia	0·110 „
Potash and soda	0·382 „
Carbonic acid (in combined state)	0·374 „
Sulphuric acid	0·275 „
Chlorine	0·338 „
Silica	0·140 „
Precipitate by ammonia from acid solution	0·080 „
Organic matter and loss	1·775 „
Total	4·000

The acids and bases may be arranged thus:

Carbonate of lime	0·850 grains.
Sulphate of lime	0·121 „
„ magnesia	0·323 „
Chlorides of potassium and sodium	0·670 „
Phosphate of lime and iron	0·080 „
Silica	0·140 „
Organic matter and loss	1·816 „
	4·000

In this scheme, I have supposed the sulphuric acid to be increased by ·009 grain, in order to make it take up the whole magnesia. The alkalies were determined together; but in the qualitative examination, potash was readily detected in the residue of 1 gallon.

The dry residue, obtained by evaporating the water, not being deliquescent on exposure, the absence of earthy chlorides was inferred. In the precipitate by ammonia from an acid solution, the presence of lime and iron was detected, but the proof of phosphoric acid was inconclusive. Operating afterwards, however, on the solid contents of a much larger quantity of water (about 15 gallons), this acid was shown pretty distinctly. The dry residue of 1 gallon gave no indication of nitric acid when tried with sulphuric acid and sulphate of iron. Boiled with carbonate of soda, it gave distinct proof of ammonia.

The quantity of organic matter in specimen *A* was much larger than the Dee water usually contains; indeed the brown tint caused by it was very well marked. A portion kept in a glass bottle for some months, deposited a brownish sediment, and became clearer. It was then found to contain only 1 grain of matter volatile on ignition. A specimen (*B*) taken from the same part of the river on the 15th of February, 1851—the river being of its usual size, and the water clear and colourless—gave 3 grains per gallon of solid matter, of which only $\frac{4}{10}$ths of a grain were volatilized by ignition. It is in accordance with general experience that organic matter in water is least abundant during the winter season. A gallon (*C*) drawn from the laboratory pipe on the 26th of September (the water being colourless), left the same quantity of dry residue, and gave off about 0·8 grain on ignition. In experiments at different times, I have thus found the solid matter (dried at 212°) to vary from 3 to 4 grains per gallon; and the matter volatilized by a low red heat (generally reckoned organic matter, though it probably always exceeds the true organic matter in amount) to range from $\frac{4}{10}$ths to $1\frac{3}{4}$ grains.

III.—ACTION OF CLARK'S SOAP TEST ON DEE WATER.

In many trials of Dee water, taken either directly from the river, or from the laboratory pipe, the hardness was found to vary between 1°·1 or 1°·2, and 1°·75. But different trials of the same specimens have sometimes varied a little—such a variation as I have been accustomed to find in solutions of very low degrees of hardness, especially when this hardness is caused partly by magnesia. In specimen *A*, the hardness varied in three trials from 1°·1 to 1°·14. After standing a day or two, the lathers could not be renewed without a further addition of soap-test, raising the hardness thus in two of the cases to 1°·36. Taking the mean between the highest and lowest, we may assume the hardness of specimen *A* to be 1°·23; and this agrees accurately with three trials made on water drawn from the laboratory

pipe on the 28th of September, which should not have differed much from river water of the 24th. The greatest hardness observed was in specimen *B*, taken direct from the river on the 15th of February. It turned out 1°·75; but as the specimen was highly aerated, it is just possible that a little of this apparent hardness may have arisen from carbonic acid.

In specimen *A*, I distinguished the hardness caused by lime from that caused by magnesia, by means of the soap-test, as follows: A mixture of equal bulks of standard lime solution 20° and distilled water was tried, and the hardness noted. A similar mixture of same solution 20° and specimen *A* was then made, and the hardness determined. The difference was 0°·47. This, multiplied by 2 (as the Dee water operated on was only half the standard quantity), gives 0°·94, the hardness caused by lime; and subtracting this from 1°·23, the total hardness, leaves 0°·29 as the hardness resulting from magnesia. By an extended course of experiments, I had previously satisfied myself that the soap-test is not affected by any quantity of magnesia under 6° or 8°, if associated with at least 10° of lime; hence the contrivance of the above experiments. If the whole lime in the water, as given in the preceding analysis, page 125 (omitting what may exist in the precipitate by ammonia), be calculated as carbonate, the amount will correspond exactly to that indicated by the soap-test, namely, 0·94 grain; and if the magnesia, in like manner, be calculated as carbonate of lime, it will turn out 0·26 grain, differing very little from the soap-test result; and in the case of magnesia, it is to be expected that the ordinary analysis will give under the truth. The quantity of pyrophosphate of magnesia, afforded by a gallon of water (*A*), I have noted at 0·30 grain. If this be made 0·32, it will correspond exactly with the indication of the soap-test. This new application of the soap-test promises to be of considerable utility.*

IV.—COMPOSITION OF DON WATER.

Two specimens were examined. One (*A*) was taken on the 4th of October, from the river about a mile from its embouchure, quite beyond the reach of the tide. The other (*B*) was collected near the Bridge of Alford (about 35 miles up, counting the windings of the river), on the same day, and about nine hours previous to the collection

* The Culter Burn, a large tributary of the Dee, which drains the Loch of Skene and surrounding country, I found to contain at its confluence with the Dee (about 8 miles up), on the 26th of September, 6 grains of fixed salts per gallon, with 2 or 3 grains of organic matter additional. Hardness 3°·1.

of specimen *A*. The river was in its average condition. Specimen *A* was tinged brown with vegetable matter, which also affected the taste. Flocculi of organic matter were seen in it, and brown specks of iron and organic matter, speedily subsiding on rest. No air-bubbles emitted on exposure. By careful evaporation, the solid matter was found to be in the proportion of 8·64 grains per gallon, and of this there were 3·04 grains volatilized by ignition. The composition of the dry matter was as follows:

Lime	1·29 grains.
Magnesia	·34 „
Alkaline chlorides, containing 0·74 of chlorine	1·32 „
Carbonic acid (in combined state)	·96 „
Sulphuric acid	·76 „
Silica	·60 „
Precipitate by ammonia from acid solution	·38 „
Organic matter	3·00 „
Total	8·65

The acids and bases may be taken thus:

Carbonate of lime	2·18 grains.
Sulphate of lime	·17 „
„ magnesia	1·00 „
Chlorides of potassium and sodium	1.32 „
Phosphate of lime and iron	·38 „
Silica	·60 „
Organic matter	3·00 „
Total	8·65

Specimen *B* was very faintly tinged with vegetable matter, and contained some floating specks of the same. On evaporation, it left at the rate of 5· grains solid matter per gallon, of which 3·8 were fixed salts, and 1·2 volatile (organic matter).

Hardness of Don Water.—The soap-test with specimen *A* gave 3½°, with *B*, 2½°. The hardness of *A*, calculated from the above table, is, for lime, 2°·32, for magnesia, 0°·82; together equal to 3°·14. The phosphates would add something to this. I had not an opportunity of applying the new soap-test process to this specimen in its original state. After being kept four months in a stoneware jar, the water was found to have increased in hardness to 4°·2. The total solid

matter per gallon had increased to 9·6 grains, while the organic matter remained precisely as at first, 3·04 grains. On applying the soap-test to separate lime or magnesia, in the manner already described, the hardness, owing to lime, was found to be 3°·4, and that from magnesia 0°·8: while the lime had thus been increased by impurity from the jar, the magnesia appears to have remained unaltered.

IV.—ACTION OF DEE WATER ON LEAD.

Under this head I have recorded about forty trials, made at different times, and on water from houses in various parts of the town; besides upwards of a dozen experiments with lead bars in specimens of water not previously in contact with lead. In the sequel, I shall make such a selection from these trials as may serve to bring out the conclusions arrived at.

Mode of operating.—The test used was sulphuretted hydrogen; the water being previously acidulated with hydrochloric acid, and the gas transmitted a sufficient length of time. In the earlier trials I used only one or two pints of each specimen, but it soon became apparent that much greater delicacy was attainable by employing a larger quantity. In proceeding with the experiments, therefore, I operated uniformly on a gallon, contained in a glass beaker, of such dimensions that the water had a depth of 10½ inches. By placing the beaker on a piece of white paper, and looking downwards, I was able to appreciate a very slight change in tint. Another similar vessel, with the same quantity of water, was always placed by the side of the first, for the sake of comparison. In estimating the quantity of lead present in any case, I had recourse to a very simple expedient. A solution of lead was prepared of definite strength; chloride of lead was used at first, but afterwards pure nitrate, as more convenient. 1·6 grain of nitrate was dissolved in 1000 grains of distilled water, so that the solution contained 1 of metallic lead in 1000. From an accurately graduated measure, I dropped this solution into a gallon of water containing no lead, until, on transmission of sulphuretted hydrogen, the same depth of tint was developed as in the particular case on trial. Having come as near as possible to the right quantity in this way, I commonly then made a new mixture, adding at once the ascertained quantity of lead to a gallon of water, and transmitting the gas. If the two trials corresponded, the experiment was finished, but in case of any discrepancy, the trial was repeated. This method, I believe, will give very accurate results, until the quantity of lead exceeds ¼ grain per gallon, when the colour gets so dark that slight

differences cannot well be discriminated. I found that $\frac{1}{100}$th of a grain of lead, added to a gallon of pure clear water, gave a tint quite perceptible, that is, 1 of metallic lead in 7 millions; and a less quantity could readily be distinguished by careful comparison. Even in specimens previously containing a considerable proportion of lead, the difference of $\frac{1}{100}$ of a grain was plainly visible. Here is an instance: A gallon of Dee water, taken from a leaden pipe, having given a certain tint with sulphuretted hydrogen, a gallon of Dee water, not containing lead, was placed beside it, and 80 grains of the standard solution (containing 0·08 grain of lead) well mixed. By the action of sulphuretted hydrogen, the tint produced was a little lighter than in the other; 10 drops more made the tints equal; and again 10 drops rendered the last somewhat darker than the first. Now every 10 drops of solution contained $\frac{1}{80}$ of a grain of metallic lead.

The preliminary acidulation with hydrochloric acid is very essential when the water under trial happens to contain any iron. In some spring waters that I examined, there was a blackening caused by sulphuretted hydrogen, from the presence of iron in combination with organic matter. Acidulation with hydrochloric acid entirely prevents this blackening, or destroys it after it has been produced, leaving a milkiness in the water, from deposition of sulphur. To ascertain if the hydrosulphuric acid test would be affected by a minute quantity of iron, I dissolved 1 grain of the pharmaceutical ammonio-tartrate (which would contain about $\frac{1}{7}$th of a grain of metallic iron, or $\frac{1}{5}$th grain of red oxide) in a gallon of water. The solution had a greenish-yellow tint. On transmitting the gas, there was no change for some time, but ultimately an evident darkening, with deposition of sulphur.

Selection of trials of Water from House-pipes (*lead*). — Specimens taken during the day, when the water would be in its usual condition, unless stated otherwise.

1. Pipe about 16 yards long—no cistern—no indication of lead.

2. Pipe 12 or 15 yards—no cistern—specimen drawn first in the morning showed a trace of lead (less than $\frac{1}{100}$ of gr. per gallon), specimen drawn at mid-day—no lead.

3. Pipe about 36 yards—no cistern—about $\frac{1}{30}$ of gr. metallic lead per gallon. On another occasion, this pipe gave rather more lead.

4. Pipe upwards of 100 yards—no cistern—tried on different days, the quantity of lead varied from $\frac{1}{30}$ to $\frac{1}{40}$ gr. per gallon.

5. Pipe 16 or 18 yards—small cistern—lead under $\frac{1}{100}$ gr. per gallon.

6. Pipe about 24 yards—cistern—several families supplied, and much water used—no indication of lead.

7. Pipe about 15 yards—cistern— $\frac{1}{50}$ gr. of lead per gallon.

8. Pipe about 30 yards — cistern — about $\frac{1}{35}$ gr. of lead per gallon.

9. Pipe about 100 yards, leading into cistern with about two cubic feet of water,—$\frac{1}{20}$ gr. of lead per gallon. This being the largest quantity I have found in any water in ordinary domestic use, I made particular inquiries in regard to the health of the family. Nothing unusual had ever been noticed, except that, on coming into town for the winter (the family lived in the country during summer), the children speedily lost colour. This, of course, is usually attributed to the *air* of the town, but it would be worth inquiring how much of the effect in such cases is due to the *water*. This case, however, shows that water containing $\frac{1}{20}$th of a grain of metallic lead per gallon (equal to $\frac{1}{15}$ gr. carbonate), may be used habitually without any notable injurious results. Mr. W. Herapath related a case in the "Times" (14th Sept. 1850), where $\frac{1}{9}$th of a grain of lead per gallon deranged the health of a whole community. The limit of the deleterious action would seem thus to be somewhere between $\frac{1}{10}$th and $\frac{1}{20}$th of a grain.

10. The leaden pipe supplying Marischal College afforded some instructive points. It is upwards of 100 yards long. Specimens of water, drawn before entering any of the cisterns, contained, as stated in case 4, from $\frac{1}{30}$ to $\frac{1}{40}$ of a grain per gallon. About the middle of the pipe, a branch is taken off to the porter's house, where it discharges into a small cistern. Water taken from this at different times contained $\frac{1}{25}$ to $\frac{1}{30}$ of a grain of lead per gallon. The college pipe near its termination supplies a cistern containing usually about 10 cubic feet of water. A specimen taken direct from this cistern I found to contain $\frac{1}{12}$ or $\frac{1}{13}$ of a grain of lead. A specimen taken at the same time from a pipe that proceeds from this cistern about 20 yards, contained $\frac{1}{11}$ of a grain. The pipe was allowed to run a good deal before the specimen was drawn. Tried at various times, this pipe afforded from $\frac{1}{8}$ to $\frac{1}{14}$ of a grain of lead per gallon. Another pipe from the same cistern, after remaining a day or two unused, contained sometimes $\frac{1}{5}$, or even $\frac{1}{4}$ of a grain per gallon.

Selection from Experiments with Lead Bars.—1. Bar of bright lead, immersed (to the extent of 23 square inches of surface) in 2 pints of Dee water—left 48 hours—water remained clear—no deposit—a thin whitish film had formed on lead. The water, after filtration through double filter, contained about $\frac{1}{150}$ of a grain of lead per gallon.

2. Parallel experiment with distilled water: water speedily became

milky—abundant white deposit. Passed several times through double filter, but milkiness not removed. After standing two days, the white matter subsided, and the water then filtered clear. No lead whatever in solution. (The oxide was probably entirely converted into insoluble carbonate by exposure.)

3. Bar No. 1 immersed, without cleaning, in 2 pints of Dee water, and left 48 hours—no deposit. Passed through double filters, the water contained about $\frac{1}{20}$ of a grain of lead per gallon.

4. Bright bar, in 3 pints of Dee water—32 square inches immersed—left 24 hours—filtered—contained trace of lead.

5. Same bar, without cleaning, in 2 pints—26 inches immersed—left 48 hours—filtered—contained $\frac{1}{20}$ of a grain of lead per gallon.

6. Lead bar tarnished in air, immersed (to 30 square inches) in 3 pints—left 48 hours—filtered—$\frac{1}{30}$ of a grain of lead per gallon.

7. The bars used in experiments 5 and 6, were placed, without cleaning, in similar quantities of water, and left 48 hours—not filtered. The water from bar 6 contained about $\frac{1}{10}$ of a grain of lead per gallon. The water from bar 5 contained more.

8. The bar from experiments 5 and 7 being again immersed without cleaning, and left 48 hours, the water unfiltered contained much more lead than in last experiment—about $\frac{1}{6}$ of a grain per gallon.

9. Same bar, left 48 hours, in 2 pints—water passed through double filter, contained about $\frac{1}{10}$ of a grain (or rather more) of lead per gallon.

10. Bar of bright lead, immersed in 2 pints of Dee water for 4 days. The water had been kept for some time in a jar, in a warm room, so that a great part of the air had escaped from it. After filtration the water contained a mere trace of lead. Bar immersed again, without cleaning, in other 2 pints of same water, and left for 2 days. Water (filtered) contained more lead than in last case, but still not much.*

From these experiments, it appears that Dee water acts more readily upon tarnished or crusted lead, than upon the bright metal; that the lead taken up by the water is separated to a small extent by paper filters; and that when a crusted bar is immersed for a certain time in water, dried, and immersed again for the same time, the action is greater the second time than the first; dried and immersed a third time, the action is still greater. (So that a lead cistern, alternately filled and

* The lead used in these experiments was the kind commonly employed for lining cisterns—7 or 8 lbs. to the square foot. Fresh portions of Dee water, not previously contaminated by lead, were used in each case.

emptied, is more unsafe than one kept constantly at the same level, both being freely exposed to the air.)

From the foregoing observations I conclude that the action of Dee water on lead is comparatively feeble, but yet that by prolonged contact, more especially when there is free exposure to air, as in cisterns, a dangerous quantity of that metal may be taken up. With lead pipes of moderate length, and no cisterns, no danger whatever is to be apprehended. With small cisterns, and a pretty constant use of the water, there is also no danger; but the risk increases with the length of the pipe, the size of the cistern, and the time the water lies unused. When large cisterns are required for general domestic use, I think it would be prudent to have them lined with gutta percha or some other innocuous material. With an uninterrupted supply, such as is enjoyed in Aberdeen, and with an improved form of tap, cisterns might probably to a great extent be dispensed with.

In some cases it has appeared to me that old pipes are more acted upon than new; the differences, however, may have arisen from impurities in the lead, or from other special causes not detected. I am also inclined to think that the action on lead depends greatly on the aeration of the water. In rainy weather, when the Dee water is coloured and contains little air, the quantity of lead dissolved in any case appears to be less than when the water is clear and well aerated. This observation has been confirmed to some extent by the experiments with lead bars, but I am not prepared to state it unreservedly as a rule.

X.—*On a peculiar Property of Ether and some Essential Oils.*

By C. F. Schönbein.

It is now a well-known fact that phosphorus, on being put, under certain circumstances, in contact either with pure oxygen or atmospheric air, produces a highly oxidizing agent, capable of discharging the colour of indigo-solution, eliminating iodine from the iodide of potassium, transforming the yellow prussiate of potassa into the red salt, changing a number of metallic sulphides into sulphates, &c.

From the statements hereafter made, it will appear that, besides phosphorus, there are some other oxidable matters enjoying the same property.

I.—ETHER.

A large colourless glass bottle being charged either with pure oxygen gas or atmospheric air, and holding some recently prepared pure ether, was put up in a room receiving but diffused light, and now and then shaken. After the lapse of four months, the ether exhibited the following properties:

1. No action upon blue litmus-paper.

2. Water fairly black by indigo solution, on being shaken with the ether became colourless, more rapidly so on heating the mixture than in the cold. Strips of linen fairly dyed by indigo solution and suspended within a large bottle containing some ether, were completely bleached within a couple of days.

3. The ether, on being put in contact with pure phosphorus, rapidly turned sour, phosphorous acid being formed.

4. The ether, on being shaken with a solution of pure iodide of potassium, turned brownish-yellow, acquiring the property of colouring dark blue the paste of starch.

A dry strip of my ozone test-paper (prepared by drenching white filtering paper with a thin paste of one part of iodide of potassium, 10 parts of starch, and 200 parts of water) moistened with the ether, soon assumed a brown, and if then wetted with water, a dark-blue colour. The same test-paper, being moistened with water and suspended in the ether vapour, turned dark blue within a few hours.

5. The ether, on being shaken with a solution of pure sulphate of protoxide of iron, caused the transformation of that salt into the basic and acid sulphate of sesquioxide of iron, more rapidly so on heating the mixture than in the cold.

6. The white cyanide of iron (obtained from the yellow prussiate of potassa and pure sulphate of protoxide of iron), on being shaken with the ether, instantly turned dark blue.

7. A colourless solution of the yellow prussiate of potash, on being shaken with the ether, turned yellow (in consequence of the formation of the red salt).

8. White filtering paper, coloured brownish by sulphide of lead, on being immersed in the ether, turned white again within a couple of hours, the sulphide being transformed into the sulphate of lead. Strips of sulphide of lead paper suspended within bottles holding some ether, appeared completely bleached in a few hours, light being entirely excluded.

9. Filtering paper coloured yellow by sulphide of arsenic and immersed in the ether, was bleached in a few days.

10. Aqueous sulphurous acid, on being shaken with a sufficient quantity of the ether, was rapidly and completely transformed into sulphuric acid.

11. The ether, on being repeatedly distilled over lost its oxidizing powers.

It is hardly necessary to say, that recently prepared ether, or old ether carefully preserved from contact with atmospheric air, leaves the ozone test-paper entirely unchanged, and exhibits no oxidizing action whatsoever.

It being very likely that the oxidizing principle we have traced in ether enjoys peculiar physiological properties, ether having been for some time in contact with atmospheric air, ought perhaps not to be used for medical purposes. It is not impossible that some of the deleterious effects which have been observed to be produced by the inhalation of ether vapour are connected with our oxidizing principles.

II.—ESSENCE OF TURPENTINE.

Different as this oil is from ether as to its chemical constitution, it nevertheless in some respects resembles the last-named substance. Oil of turpentine, like ether, at the common temperature, takes up oxygen, giving rise to the formation of acetic acid, and a highly oxidizing matter. A large colourless glass bottle being charged either with pure oxygen gas or atmospheric air, and holding some fresh oil of turpentine, was put up for about four months* in a room receiving only diffused light, and shaken and opened now and then; after this

* Since this paper was written, I have ascertained that oil of turpentine may in a much shorter time be oxygenated to a considerable extent. Shaking frequently the essence with insolated oxygen or atmospheric air will lead to that result. In the way indicated, I have succeeded in preparing within a couple of weeks oxygenated oil of turpentine, which is capable of discharging the colour of 36 times its weight of my standard indigo solution. Pure oil of turpentine having for the same length of time been kept in contact with dark oxygen, does not yet exhibit any perceptible degree of oxidizing powers. Hence it appears that light, independent of heat, very much favours the oxygenation of the oil of turpentine, &c.

To convince yourself of that action of light, cover the bottom of two white bottles holding atmospheric air with chemically pure oil of turpentine, suspend in either of them a moist band of my ozone test-paper, darken one of these vessels and expose the other bottle to the action of direct solar light, and you will within a few minutes perceive the edges of the test-paper suspended in the insolated bottle to assume a violet tint, and the whole paper turn dark blue in an hour or fifty minutes, whilst the test-paper in the dark bottles has during the same space of time not undergone any perceptible change.

Strips of linen dyed by indigo solution will remain unchanged in the darkened bottle, and be bleached in the insolated one, &c.

time, the essence had acquired the property of reddening strongly blue litmus-paper, and a very strong oxidizing power, as will appear from the following statements:

1. Water rather strongly blued by indigo-solution, on being shaken with the oil, soon lost its colour, more rapidly so at a raised temperature than in the cold. One gramme of the oil, on being poured into a boiling mixture of 100 grms. of water and 5 grms. of a strong indigo-solution, discharged the deep-blue colour of the liquid as rapidly and completely, as if chlorine or bromine had been used instead of essence of turpentine; and the oxidizing power of the oil was not yet entirely exhausted, it being still able to destroy 3 grms. more of the indigo-solution, so that the oil could destroy fully eight times its own weight of the strong solution. I hardly need say that to obtain the full oxidizing effect of the oil upon the indigo-solution, it is required to shake both the liquids briskly together while they are heated. Moist strips of linen coloured light blue by indigo-solution, on being immersed in the cold oil, became white in two hours, and in the hot essence almost instantaneously. Bits of linen cloth coloured light blue by indigo-solution, on being suspended within large bottles holding some oil, were completely bleached within a few days.

2. Atmospheric air being entirely excluded, the oil when put in contact with pure phosphorus, rapidly produced phosphorous acid with some phosphoric acid.

3. The oil, on being mixed up with some acetic acid and shaken with minutely divided silver, soon produced appreciable quantities of acetate of silver. Heat being applied, the formation of the acetate was more rapid and abundant. Mercury and copper were likewise oxidized by the oil and transformed into acetates.

4. The oil took up sulphurous acid gas, immediately transforming it into sulphuric acid. Aqueous sulphurous acid, on being shaken with a sufficient quantity of the oil, was likewise turned into sulphuric acid.

5. The oil, on being shaken in the cold with a solution of iodide of potassium, assumed a reddish tint, whilst the saline solution turned brownish-yellow. On heating and shaking both the liquids together, the essence became deep brownish-red, from the iodine being eliminated and taken up by the oil.

Dry bits of ozone test-paper moistened with the oil soon became brown, turning dark blue if then plunged in water. The said test-paper being moistened with water and suspended in bottles whose bottom was covered with the oil, turned dark blue within the space of a few hours.

The test-paper mentioned affords the most convenient means of ascertaining the presence of the oxidizing principle in ether, oil of turpentine, &c. The deeper the brown or blue colour which the paper acquires on being drenched with the liquids examined, the richer are they in the oxidizing matter.

6. A strong solution of pure sulphate of protoxide of iron, on being heated and shaken with the essence, was very rapidly transformed into the basic and acid sulphate of sesquioxide of iron. The same action took place in the cold. I hardly need mention that the protochloride of iron underwent a similar change.

7. The white cyanide of iron above-mentioned, on being shaken with the oil, turned instantaneously dark blue, just as if ozone, peroxide of hydrogen, bromine, chlorine, nitrous or nitric acid, had been added to the said compound.

8. A nearly colourless solution of the yellow prussiate of potassa, on being shaken in the cold, with the essence, turned deep yellow, and was rapidly transformed into the red salt at the boiling-point of water.

9. Minutely divided sulphide of lead, suspended in water, on being heated and shaken with the oil, turned white, sulphate of lead being formed.

Strips of filtering paper, rather strongly coloured by sulphide of lead, turned completely white in the cold oil within a couple of hours, and almost instantaneously in the hot essence.

Strips of such paper suspended in bottles, being covered with the oil, were completely bleached within a couple of hours, although light was entirely excluded.

10. Minutely divided sulphide of arsenic, suspended in water, on being heated with the essence, rapidly disappeared, sulphuric and arsenious acids being formed.

11. A specimen of oil of turpentine, capable of destroying thirty-two times its own weight of the strong indigo solution, on being heated almost to its boiling point for nearly a quarter of an hour, lost 250 per cent of its oxidizing principles. If half the bulk of the same specimen of essence was distilled over, this portion of the oil could but destroy the tenth part of its own weight of the standard indigo-solution. This fact proves that heat tends to destroy the oxidizing principle.

I must not omit to state, that all the specimens of essence of turpentine I have as yet met with in commerce and examined, exhibit oxidizing properties, but in very different degrees. Some of them were able to destroy not quite the sixth part of their own

weight of the standard indigo-solution; others, half their weight; others, twice their own weight, &c. The specimen of essence of turpentine, to which the preceding statements refer, was the richest in the oxidizing matter which I have yet met with, being able to discharge the colour of fully thirty-two times its own weight of the standard indigo-solution. I may therefore say that the rates of the oxidizing powers of the two extreme oils examined were as 1 : 192. I further found that in all cases, the one which had been longest exposed to the action of pure oxygen gas or atmospheric air, was found to possess the greatest oxidizing power.

III.—OIL OF LEMONS.

Numerous experiments, made with genuine essence of lemons imported from Sicily, proved to me that this oil enjoys to a high degree the power of engendering a powerful oxidizing principle, when put in contact with oxygen or atmospheric air; for with such oil I could produce all the oxidizing effects above mentioned. In examining a variety of specimens of that essence, I found that all of them had oxidizing powers, more or less, according to the length of time during which they had been in contact with the atmospheric air. One specimen I met with in commerce was capable of discharging the colour of $2\frac{1}{2}$ times its own weight of the standard indigo-solution. I must not omit to mention here the curious fact that cork-stoppers, having for some time been used to close up bottles containing ether, oil of turpentine, or essence of lemons, appear bleached and attacked in the same manner as if they had been fixed on vessels holding ozone, bromine, chlorine, or nitric acid. It is superfluous to say that the bleaching of those stoppers is due to the same oxidizing agent which, according to the preceding statements, destroys the colour of indigo, &c.; but I must not omit to state that, on examining in a commercial house of Bâle, in which large stores of essential oils are kept, all the cork stoppers closing up the bottles, I found many of them strongly bleached and attacked. This makes me almost certain that on further examination, besides essence of turpentine and lemons, other volatile oils will be found to possess the power of engendering an oxidizing principle on their being put in contact with oxygen. Nay, I have reason to believe that even substances, very different in chemical constitution from essential oils, will behave like essence of turpentine, &c.

How far light is concerned in the formation of the oxidizing matter above spoken of, I do not yet venture to decide. A variety of

facts make me inclined to believe that light favours very much the generation of that principle. I hope, however, to be able to speak with certainty about the subject before long.

THEORETICAL VIEWS ON THE FACTS ABOVE STATED.

If I am asked what the oxidizing principle formed in ether and the essential oils on their contact with common oxygen is, I cannot as yet answer that question otherwise than by conjecture, for all my endeavours to insolate that principle have failed. All the substances acting upon it are of an oxidable nature, and yield products identical with those which are obtained from the very same oxidable matters on their being subject to the action of ozone. Phosphorus and a number of metals are oxidized, sulphurous acid converted into sulphuric acid, metallic sulphides transformed into sulphates, &c. I cannot therefore help conjecturing that the oxidizing principle in question is nothing but oxygen, being in that chemically exalted condition in which we know it to exist in ozone. This opinion appears to me to receive an additional support from the fact that ether, oil of turpentine, &c., on being shaken with strongly ozonized air, rapidly take up all the ozone, acquiring by that treatment the same oxidizing properties as are gradually developed on putting ether or oil of turpentine in contact with common oxygen.

With reference to the question before us, it seems to me that the behaviour of guajacum is worthy of our consideration.

An alcoholic solution of that matter turns blue on being shaken either with strongly insolated oxygen, or ozonized air, or a number of metallic peroxides, such as that of lead, manganese, &c. Hence I conclude that blue guajacum is but a loose compound of the resinous matter with chemically excited oxygen, being comparable to the loose blue compound formed by iodine with starch.

According to my former researches, it is a fact that the excited oxygen which colours blue guajacum may easily be taken away again from the resinous matter, and transferred to a number of readily oxidable matters, such as phosphorus, sulphuretted hydrogen, sulphurous acid, metallic sulphides, &c., whence it comes that the matters mentioned have the power of discharging the blue colour of the guajacum solution, just in the same way as the very same oxidable substances discharge the colour of the aqueous solution of iodurettted starch. From the preceding statements, it appears that the blue alcoholic solution of guajacum may indeed, as to its oxidizing powers, be com-

pared to the oil of turpentine, &c., which has for some time been put in contact with common oxygen or atmospheric air.

There is another fact to be mentioned bearing upon our question. The chemically excited oxygen loosely united to guajacum gradually exerts an oxidizing influence upon the oxidable constituent parts of the resinous matter. According to my experiments, the solid guajacum, as obtained from the dark blue tincture by mixing it up with water, preserves for any length of time its blue colour when kept in the shade, whilst the same blue guajacum if dissolved in alcohol, gradually loses its colour. Recently prepared tinctured guajacum coloured as deep blue as indigo-solution by the means of peroxide of lead or manganese, at the common temperature, reassumes its original brownish-yellow tint in the course of a few hours. If, in the same manner as before, that tincture be re-blued, then suffered to lose its colour again spontaneously, and these colourings and spontaneous discolourings repeated a certain number of times, the tincture will at last be changed so as to become incapable of being blued any more by peroxide of lead or any other means. This fact proves, that by the proceedings described, the chemical constitution of guajacum is altered, no doubt in consequence of a gradual oxidizing action produced by the excited oxygen existing in the tincture, upon the oxidable constituent parts of the resinous matter. Now guajacum being able to form a loose compound with chemically excited oxygen, why should not ether, oil of turpentine and a number of other substances be capable of entering into similar combinations? and if the excited oxygen loosely associated to guajacum, gradually act upon the constituent parts of that resin, why should not the excited oxygen, stored up in ether, oil of turpentine, &c., produce oxidizing effects upon these matters, and give rise to the formation of carbonic and acetic acids, acetic ether, resins, &c.?

As already mentioned, I am inclined to think that the excited oxygen contained in the blue tincture of guajacum, is in a state of combination similar to that in which iodine exists in ioduretted starch, whence it comes that common guajacum dissolved in alcohol, is as delicate a test for excited oxygen, as paste of starch proves to be for free iodine. Now, as that body is capable of loosely associating itself not only to starch, but to many other organic substances, without producing blue-coloured compounds, so may excited oxygen enter with many organic matters into loose combinations similar to that which it forms with guajacum, without colouring those matters blue.

There is another analogy existing between the organic solution of ioduretted starch and the blue tincture of guajacum, which, in my opinion, is worthy of being pointed out here. Both the liquids spontaneously and gradually discharge their blue colour. Now, if the solution of starch be re-blued by iodine, then suffered to lose its colour again, then blued a third time and spontaneously discoloured, and so on, the dissolved starch will at last lose its property of being coloured blue by iodine. Hence it follows, that the chemical constitution of starch undergoes some change analogous to that suffered by guajacum. In one case, the iodine being loosely associated to starch disappears, hydriodic acid being formed, and no doubt some oxidizing action produced upon the oxidable constituent parts of starch; in the other case, excited oxygen disappears, the guajacum likewise suffering oxidation. Strange as it may sound, I do not hesitate to say that I see in both the cases mentioned one and the same action. If I should be requested to give my full opinion about the nature and formation of the oxidizing principle met with in ether, the essences of turpentine, lemons, &c., it would be as follows. Ether, oil of turpentine, &c, on taking up common oxygen, cause (assisted by light) in a manner as yet entirely unknown to us, in that body a change of condition, similar to that brought about in common oxygen under the influence of phosphorus or electricity. The oxygen thus modified enters into a loose combination with the oil of turpentine, &c., and it is only then that the excited oxygen begins to produce real oxidizing effects upon the constituent parts of the organic substances with which it happens to be associated, *i. e.* to engender carbonic acid, acetic acid, resins, &c., just as is the case with phosphorus, if it be placed in contact with atmospheric oxygen. The first action produced by phosphorus upon common oxygen, is to transform the latter into ozone, and this work being performed, the acidification of phosphorus begins to take place, not at the expense of common, but of ozonized oxygen; and as, under given circumstances, phosphorus is capable of producing more ozone than it can take up, it becomes by that very behaviour as, excellent a means of engendering free ozone, as oil of turpentine, &c. Under given circumstances, more oxygen is brought into its chemically exalted condition by the oxidable liquids mentioned than they are able to consume; and hence it comes that, on their being placed in contact with common oxygen, they are storing up excited oxygen to a great extent. The only difference existing between the two cases of the formation of ozone seems to be this: In the first case, all the

ozone formed, and not employed for the oxidation of phosphorus is, on account of its gaseous state, dispersed into the ambient air, whilst in the second case, the surplus of the excited oxygen engendered is kept simply dissolved by the essential oils, &c., or enters into a loose combination with them.

Now if it be a fact that, previously to its having been transformed into ozone, common oxygen cannot chemically unite even with phosphorus (at the common temperature) and if it be highly probable that the slow oxidation which ether, oil of turpentine, &c., undergo at the common temperature, is effected, not by common, but by excited oxygen, I think we may be allowed to conjecture that at the common temperature, ordinary oxygen, as such, is not able to combine chemically with any matter, and all the slow oxidations are preceded by a transformation of common or inactive oxygen into ozonized or active oxygen. The fact, that we do not in all cases of slow oxidation perceive that change of condition of the oxygen employed, as we do it in that of phosphorus, oil of turpentine, &c., may possibly be due to a difference in the intensity with which different oxidable matters (capable of undergoing slow oxidation) exert their modifying influences upon common oxygen. Some of those substances may have the power to engender more ozone than they can consume, others may produce just as much as they take up, or less.

As to phosphorus, that body may easily be conditioned so as to make it consume all the ozone it engenders, in the very moment of its formation. Phosphorus placed within moist atmospheric air will, at the freezing-point of water, or thereabout, begin to shine in the dark and be slowly oxidized, without yielding, however, the slightest trace of free ozone, as may be easily ascertained by my test-paper. On raising the temperature to about 10° C. the phosphorus will shine more vividly, be oxidized more rapidly, and yield free ozone. From this fact, we learn that even one and the same body may be slowly oxidized either with or without the appearance of free active oxygen.

Binoxide of nitrogen is no doubt the most readily oxidable matter we are acquainted with; for it unites with common oxygen even at very low temperatures to form hyponitric acid. Even in that case, I am inclined to believe that previously to its entering into a chemical combination with that binoxide, the common oxygen undergoes a change of condition. However that may be, it is a fact that the oxygen taken up by the binoxide exists in a condition in which it causes a variety of oxidizing effects very similar to those

produced by ozone itself. Hence it comes that some years ago several continental chemists declared ozone to be nothing but hyponitric acid.

In concluding this paper, I say that if anybody is able to give a better opinion about the facts described in it than mine is, I shall gladly accept and adopt it; for I care very little for my views, but a vast deal for truth.

XI.—*An Analysis of Sediment deposited from the River Nile in Lower Egypt.*

By Matthew W. Johnson, Esq.,

of the royal college of chemistry, london.

The almost proverbial fertility of the Nile valley is usually ascribed to the mud deposited upon the fields after the floods of the River. As this substance does not appear to have been hitherto analysed, I availed myself of the opportunity afforded me by Dr. Hofmann* of submitting a genuine specimen of the substance collected in the neighbourhood of Cairo, to examination.

On the qualitative analysis of the sediment, the following substances were shown to be present, viz.: sesquioxide of iron, alumina, lime, magnesia, potassa, soda, traces of manganese, silicic acid, sulphuric acid, chlorine, carbonic acid, traces of phosphoric acid and organic matter.

Quantitative analysis.—The method followed in this analysis was for the most part that which is usually adopted for the analysis of soils. Without entering into details, I may just mention that a general separation was effected by solution in hydrochloric acid, and that separate portions of the hydrochloric solution were used for the determination of the individual constituents, with the exception of the chlorine. The residue insoluble in hydrochloric acid was fused with carbonate of soda, after a special experiment with baryta had proved the absence of appreciable quantities of alkalies.

The general course of the analysis becomes sufficiently intelligible

* I am indebted to Leonard Horner, Esq., F.R.S., for the specimen in question. Engaged in a series of researches on the geology of the Nile valley, Mr. Horner was anxious to know the composition of this deposit in order to compare its constituents with those of the rocks which the river washes on its passage, and had the above specimen sent over from a friend residing in Egypt.—A. W. H.

from the following tables, in which I have arranged the experimental numbers.

TABLE I.—Behaviour with solvents :—

Soluble in water	inorganic matter	1·0566
	organic matter	0·2460
Insoluble in water	inorganic matter	93·8432
	organic matter	4·8542
		100·0000
Soluble in hydrochloric acid		31·6123
Insoluble residue		68·3877
		100·0000

TABLE II.—Quantities of sediment for analysis, and weights of the various hydrochloric solutions :—

		grms.
Quantity of air-dried sediment employed for general analysis.		14·6825
Amount of the hydrochloric solution		243·3420
Hydrochloric solution for alkalies		27·2537
Hydrochloric solution for sulphuric acid		16·8188
Hydrochloric solution for sesquioxide of iron, alumina, lime and magnesia	Exp. I.	43·0103
	„ II.	41·2290
Hydrochloric solution for sesquioxide of iron and alumina	Exp. I.	27·7310
	„ II.	28·5870
Hydrochloric solution for sesquioxide of iron	Exp. I.	13·7600
	„ II.	13·6390
Hydrochloric solution for sesquioxide of iron and alumina	Exp. I.	13·9710
	„ II.	14·9480
Quantity of air-dried sediment for chlorine	Exp. I.	8·3916
	„ II.	6·1346
Quantity of sediment for total amount of organic matter	Exp. I.	1·1993
	„ II.	1·1552
Quantity of sediment for total amount soluble in water		11·2155
Quantity of sediment for the carbonic acid	Exp. I.	3·4680
	„ II.	6·0652
Quantity of sediment for total amount of water	Exp. I.	2·2750
	„ II.	1·1993

TABLE III.—Weights of the various compounds from which the

composition of the sediment was deduced, together with that of the insoluble residue:—

Residue		9·2597
Mixed chlorides of potassium and sodium		0·0559
Bichloride of platinum and potassium		0·0997
Chloride of potassium		0·0304
Sulphate of baryta for sulphuric acid		0·0063
Sesquioxide of iron and alumina	Exp. I.	0·2166
	„ II.	0·2155
Sesquioxide of iron	Exp. I.	0·1365
	„ II.	0·1198
Carbonate of lime	Exp. I.	0·1623
	„ II.	0·1431
Pyrophosphate of magnesia for magnesia	Exp. I.	0·1507
	„ II.	0·1225
Chloride of silver for chlorine	Exp. I.	0·0884
	„ II.	0·0610
Amount of sediment left after ignition	Exp. I.	1·0445
	„ II.	1·0067
Amount of sediment left after exhaustion with water		10·2440
Amount of sediment left after exposure to 120° C.	Exp. I.	2·0970
	„ II.	1·1065

Table IV.—Analysis of the insoluble residue; quantities of residue for analysis, and weights of the various hydrochloric solutions:

Amount of insoluble residue for estimation. No. I. of silicic acid		1·9245
Amount of dry original sediment for estimation. No. II. of silicic acid		1·0237
Amount of insoluble residue for the determination of sesquioxide of iron and alumina		1·1710
Insoluble residue for the determination of lime and magnesia		1·2369
Insoluble residue for organic matter	Exp. I.	0·6312
	„ II.	1·1710
Hydrochloric solution for sesquioxide of iron and alumina		30·0019
Hydrochloric solution for sesquioxide of iron		13·0769
Hydrochloric solution for lime and magnesia		105·4800
Quantity of the above solution for Estimation I. of lime and magnesia		44·2845
Quantity used for Estimation II.		39·9557

TABLE V.—Weights of the various compounds from which the composition of the insoluble residue was deduced:

		grms.
Silicic acid	Exp. I.	1·5987
	„ II.	0·5772
Sesquioxide of iron and alumina		0·0589
Quantity of alumina dissolved by treating the fused mass with water		0·0212
Sesquioxide of iron		0·0147
Carbonate of lime	Exp. I.	0·0166
	„ II.	0·0160
Pyrophosphate of magnesia for magnesia	Exp. I.	0·0160
	„ II.	0·0149
Amount of insoluble residue left on ignition	Exp. I.	0·6112
	„ II.	1·1400

TABLE VI.—Calculated results of analysis:—

Anhydrous sediment:

	per cent.
Silicic acid =	56·87
Sesquioxide of iron =	13·19
Alumina =	12·11
Lime =	5·43
Magnesia =	2·73
Potash =	1·26
Soda =	0·89
Carbonic acid =	1·37
Chlorine =	0·27
Sulphuric acid =	0·22
Organic matter =	5·53
Traces of phosphoric acid.	
Loss =	0·13
	100·00

TABLE VII.—Portion soluble in hydrochloric acid:

	Air-dried sediment			Anhydrous sediment.
	Exp. I.	Exp. II.	Mean.	
Sesquioxide of iron	10·5976	10·0943	10·35	11·22
Alumina	5·9690	6·4723	6.22	6·75
Lime	3·4986	3·6758	3·59	3·89
Magnesia	2·1154	2·0466	2·08	2·26

	Air-dried sediment			Anhydrous sediment.
	Exp. I.	Exp. II.	Mean.	
Potassa			Exp. I. 1·16	1·26
Soda			Exp. I. 0·82	0·89
Carbonic acid . .	1·3264	1·2035	1·26	1·37
Silicic acid			Exp. I. 0·70	0·76
Sulphuric acid . . .			Exp. I. 0·21	0·22
Chlorine . .	0·2598	0·2445	0·25	0·27
Organic matter .	3·1019	3·4307	3·27	3·54
Water . . .	7·8240	7·7380	7·78	—

Portion insoluble in hydrochloric acid:—

Silicic acid . .	52·1832	51·2958	51·74	56·10
Sesquioxide of iron . . .			Exp. I. 1·81	1·97
Alumina			Exp. I. 4·95	5·37
Lime . . .	1·5753	1·2593	1·42	1·54
Magnesia . .	0·4229	0·4433	0·43	0·47
Organic matter .	1·9983	1·6695	1·83	1·99
Loss			0·13	0·13
			100·00	100·00

In the following table the bases and acids are arranged according to their probable existence in the sediment.

TABLE VIII.—Anhydrous sediment.

Portion soluble in hydrochloric acid:—

	per cent.	
Sesquioxide of iron . .	11·22	
Alumina	6·74	
Carbonate of lime . .	3·12	
Sulphate of lime . . .	0·38	
Lime	1·99	
Magnesia	2·26	
Chloride of potassium . .	0·57	
Potash	0·90	
Soda	0·89	
Silicic acid	0·76	
Organic matter . . .	3·54	
		32·37

Insoluble portion :—

Silicic acid	56·10	
Alumina	5·37	
Sesquioxide of iron . .	1·97	
Lime	1·54	
Magnesia	0·47	
Organic matter . . .	1·99	
Loss	0·19	
		67·63
Soluble portion . . .		32·37
		100·00

Provided the specimen examined represents the average composition of these deposits, it is difficult to say from which of the constituents its fertilizing power is derived. Still the great amount of organic matter, five and a half per cent, cannot be without influence on the processes of vegetation; and, moreover, its physical condition, its remarkable state of comminution, seems particularly favourable to its absorption by plants. The quantity, too, of alkalies which is present must exert a highly beneficial action upon their growth.

This specimen of sediment was accompanied by several bottles of Nile water; unfortunately the quantity was too small for a complete analysis, I must therefore confine myself to the following remarks regarding it.

It possessed a slight odour of sulphuretted hydrogen, but failed to blacken acetate of lead. Its taste was soft, and it had no reaction upon litmus-paper. Chloride of calcium and ammonia indicated mere traces of carbonic acid.

The qualitative analysis of the residue, left on the evaporation of about a pint and a half of water, pointed out the presence of the following substances, sesquioxide of iron, lime, magnesia, soda, silicic acid, carbonic acid, sulphuric acid, chlorine, and organic matter. The quantity of substance operated on was too minute to establish the presence of alumina, manganese, potassa, ammonia, phosphoric acid, nitric acid, apocrenic or crenic acids.

On evaporating 454·716 grms. of the water to dryness, it furnished 0·1097 grm. of solid residue, which proved, on ignition, to contain 0·0310 grm. of organic matter. According to these results, an imperial gallon contains 1·09 grm. or 16·82 grains of solid matter, consisting of 0·78 grm. or 12·04 grains of inorganic matter and 0·31 grm. or 4·78 grains of organic matter.

Its hardness, according to Prof. Clarke's soap-test method, was then taken.

In six experiments the following measures of soap-test were required to produce on the surface of the water a froth that would last five minutes:—

Exp. I.	II.	III.	IV.	V.	VI.	Mean.
19·4	19·4	19·6	19·6	19·6	19·4	19·5

This corresponds to 9·05 degrees of hardness.

APPENDIX.

Since reading to the Chemical Society my paper on the Nile Sediment, I have found that it has been analysed before: by Regnault, in 1812; Lassaigne, 1844; and by MM. Lajonchère, Payen and Poinsot, in 1850.*

The following table shows the results of *their* analysis as compared with my own:—

Anhydrous sediment:

	Lassaigne.	Lajonchère.	MM. Payen & Poinsot.	Johnson.
Silicic acid	47·5	48·9	56·0	56·8
Sesquioxide iron	15·2	12·4	13·6	13·1
Alumina	27·1	26·5	11·1	12·1
Carbonate of lime	4·3	4·0 (Carb. and Sulphate Lime.)	9·8 (Carb. and Sulphate Lime.)	6·9
Carb. Mag. & Mag.	2·5	2·1	4·1 (MgO)	2·7
Alkaline chlorides	.	0·6	0·1	2·3
Organic matter	3·1	5·0	4·9	5·5
Phosphoric acid	.	.	.	traces.

XII.—*Notice of a Specimen of Chlorobromide of Silver from Chili.*

By Colonel Philip Yorke, F.R.S.

The specimen to which this notice relates was brought from Chili by Vice-Admiral Sir George Seymour, G.C.H. It was an irregular mass, weighing very nearly 60lbs. Its general aspect was that of a red ochraceous substance, which here and there contained portions of quartz. On close examination, however, the mass was found to be partially coated, and in several directions traversed, by veins of a

* J. Pharm. [3] V, 468, and idem XVII, 46.

sectile, waxy substance, which, when cleaned from ochre, was nearly black externally, but internally of a greenish-yellow colour, translucent and crystalline. The veins varied in thickness from $\frac{1}{4}$ of an inch to microscopic minuteness. The ochreous matter contained occasionally very small cubic crystals disseminated in it, and the coating was in some parts marked by impressions indicating some of the more complicated modifications of the cube. The specific gravity of the sectile substance from a mean of three trials on fragments, cleaned as much as possible from adhering foreign matter, was found to be=5·53.*

73·4 grs. of the specimen in fragments accidentally broken off, and found in the wrapper, were fused with a mixture of the carbonates of potash and soda, and yielded a button of silver=17·4 grs. The alkaline salts dissolved in water, were found by means of solution of chlorine and ether to contain bromine.

Phosphoric acid was also detected.

ANALYSIS OF THE SECTILE SUBSTANCE.

The first analysis was attempted according to the direct method of Fresenius. A fragment weighing 19 grs. was placed on a piece of zinc with some water and a few drops of sulphuric acid; metallic silver was obtained; and by addition of baryta water to the liquid, and subsequent evaporation to dryness and treatment with absolute alcohol, the saline matter was divided into two portions, one soluble and the other insoluble in that menstruum; these salts then dissolved in water, gave by precipitating with nitrate of silver, bromide and chloride of silver; but as a quantitative analysis the results were not satisfactory.

A second analysis was made by heating in a porcelain crucible 18·35 grs. of the chlorobromide with a mixture of the carbonates of potash and soda; after keeping the mixture at the point of fusion for some time, hot water added dissolved the salts; the remaining silver washed and ignited=12·28.

The alkaline solution was acidified by nitric acid and precipitated by nitrate of silver. The liquid separated from the precipitate was found to contain a trace of copper, but on testing for phosphoric acid, none was found.

The precipitate by nitrate of silver heated to the beginning of fusion in a porcelain crucible weighed 17·33 grs. Of this the

* M. Dufrénoy gives the sp. gr. of chlorobromide of silver=4·702.

greater part was removed into a bulb reduction-tube, for the purpose of subjecting it to heat in a current of dry chlorine gas; but on fusing it and suffering to cool in the glass bulb, the latter cracked from the unequal contraction of the glass and the adhering fused salt. The experiment was therefore made by transferring the substance to a little porcelain boat, which was enclosed in a tube of hard glass. The chlorine was passed over long after all appearance of the vapour of bromine had ceased. The loss on the 17·33 was then found to be = 1·92; and this multiplied by 4·221 = 8·104, the quantity of bromide of silver in 17·33; or 100 parts would consist of:

Bromide of silver . . .	46·8
Chloride	53·2

If we adopt the equivalent weights of silver, chlorine, and bromine, determined by Marignac, a substance composed according to the formula 3 Ag Cl + 2 Ag Br would contain in 100 parts:

Chloride of silver . .	53·36
Bromide of silver . .	46·64
	100·00

Calculating the quantities from the silver obtained from 18·35, the result would be:

Bromide	46·3
Chloride	53·7

This result agrees nearly with one of several analyses of different specimens of Chilian chlorobromide, made by M. Domeyko, and given by him in his memoir on some of the minerals of Chili, published in the Annales des Mines, [4] VI, 153.

XIII.—*On the Tests for Nitrates, and a new one for Nitrites.*

By David S. Price, Ph.D., F.C.S.

My attention having been directed to the detection of nitric acid in cases where, if it existed at all, its quantity could be but small, I deemed it necessary, as a preliminary step, to ascertain the merits of some of the tests usually adopted for that purpose. The experiments were confined chiefly to two reactions, generally considered the most

susceptible for nitrates; the one where the indication of the presence of nitric acid is the production of a dark violet or brown colour, caused by adding a solution of protosulphate of iron and concentrated sulphuric acid to a solution of a nitrate; the other, where it is the destructive action of nitric acid on indigo, the solution of the nitrate being made slightly acid with sulphuric acid, and then a solution of sulphate of indigo added. Before, however, detailing the results I have arrived at with respect to these tests, I shall proceed to describe a new one that has suggested itself for nitrites, but which admits, under certain circumstances, of application also for the detection of nitrates. Thinking that the addition of dilute hydrochloric acid to a solution of a nitrate in presence of iodide of potassium and starch-paste, might cause the chlorine thus liberated to act in the nascent state on the iodide, and so produce the well-known blue colour, I tried the experiment and found it to answer apparently most successfully. I was, however, surprised to find that of several nitrates employed, that of potassa was the only one with which the experiment succeeded; furthermore, that hydrochloric acid was not at all a necessary condition for the production of the blue colour, oxalic, dilute sulphuric, and even diluted nitric acids effecting the same, whilst the same diluted acids produced no change in a simple mixture of iodide of potassium and starch-paste. It was therefore evident that the action was not dependent on chlorine, but on some substance to be found in nitrate of potassa, and which will be demonstrated by the following experiments.

On distilling a few grains of nitre dissolved in five ounces of water with a small quantity of concentrated sulphuric acid, a distillate was obtained of slightly acid reaction, which when neutralised with carbonate of potassa and concentrated, and then added to a mixture of iodide of potassium, starch-paste, and dilute hydrochloric acid, was found to produce a much deeper blue colour than did a concentrated solution of the original nitrate. This led me to try the effect of the nitrites on the same test-mixture, and which I found to possess the property of liberating iodine under the circumstances described in a most remarkable degree, and which must be attributed to the reduction of hydriodic acid by nitrous acid. On subjecting the nitrate of potassa employed for the foregoing experiments to recrystallisation, the crystals then obtained were found to have entirely lost the property they originally possessed, whilst the mother-liquor retained it in a high degree, clearly showing that the peculiar action of the nitrate of potassa was to be attributed to the presence of a small quantity of nitrite. It has been shown that a very distinct indication of

nitrous acid was obtained in the distillate from ordinary nitre and sulphuric acid; in order to see if such would be the case with small quantities of pure nitre when treated with pure sulphuric acid, I repeated the experiment, employing two grains of the pure salt, six ounces of water, and half an ounce of concentrated sulphuric acid, when, after treating the distillate in the manner before described, abundant proof was afforded of the presence of nitrous acid. In all cases, therefore, where distillation is necessary in searching for nitrates, this test may be indirectly applied for them. Those substances which interfere with the formation of iodide of starch under ordinary circumstances, prevent its production also by the present test. The method of employing the test is the following: A few drops of a dilute aqueous solution of iodide of potassium (free from iodate) are mixed with a little starch-paste, and then dilute hydrochloric acid of sp. gr. 1006 added. The liquid suspected to contain a nitrite, if alkaline, must be slightly acidified with hydrochloric acid and then added to the test-mixture, when, if much nitrite be present, a dark-blue colour will be instantly produced; and if very small traces only, then the liquid first assumes a pale fawn colour, which gradually changes to that of violet, plum, and ultimately dark-blue. The extraordinary delicacy of the test will be seen from the following experiments. When water containing only the $\frac{1}{1,000,000}$th part of nitrous acid (as nitrite of soda, NaO. NO_3) is added to the test-mixture, a violet colour is almost instantly produced; with the $\frac{1}{1,500,000}$th part, the colour makes its appearance in a few seconds; with the $\frac{1}{2,000,000}$th part, after the lapse of two or three minutes; with the $\frac{1}{4,000,000}$th part, a change may be observed in twelve minutes, and with the $\frac{1}{5,000,000}$th part, a violet tint is produced in about fifteen minutes. In all these cases, the liquid rapidly assumes a dark-blue colour. By performing the experiments in a porcelain basin, the faintest indication of colour may be observed. In searching for minute traces in a very large bulk of liquid, it is advisable to add more iodide of potassium than where the volume of the liquid is small. Since performing these experiments, I find that Schönbein* has noticed the action of nitrites on iodide of potassium.

With respect to the tests for nitrates specified at the commencement of the paper, De Richemont† has found that by the employment of the first one, he was able to detect the $\frac{1}{24,000}$th part of nitric acid in a solution. The one by means of indigo has had narrower limits assigned to it; Liebig‡ who suggested it, states that the $\frac{1}{200}$th

* J. Pr. Chem. XLV, 227.
† Graham's Chemistry, 297.
‡ Gmelin's Handbuch der Chemie, I, 813.

part of nitric acid may be recognised by it, and the $\frac{1}{500}$th part, when a little chloride of sodium is added. I shall endeavour to show, that in both cases the action is in all probability due to nitrous acid, contained either originally in the substance as nitrite, or produced by the action of sulphuric acid upon the nitrate; at any rate, that nitric acid in the cold has no apparent action upon either of them. And first, as regards the test with sulphate of protoxide of iron. If sulphuric acid be added to a solution of nitrate of potassa free from all nitrite, and briskly agitated with it, so as to prevent the mixture from becoming heated, and then a solution of sulphate of protoxide of iron added, no change whatever in the colour of the liquid will ensue, even when allowed to stand for some time, which could not be the case did the action of the test depend on nitric acid. If to the same mixture, one drop of a dilute soltion of nitrite of potassa be added, a brownish colour will be immediately produced, showing the instantaneous effect of nitrous acid upon the test. If instead of keeping the mixture of nitrate of potassa and sulphuric acid cold, we gently warm it, and then add a solution of protosulphate of iron and a few drops more of concentrated sulphuric acid, a dark-violet colour will immediately appear, accompanied be an energetic disengagement of gas; the colour in this case soon disappears, owing to the heat evolved, but can readily be reinstated by a fresh addition of the protosulphate of iron. Or again, if we first add a solution of protosulphate of iron to the solution of the nitrate, and then pour in the concentrated sulphuric acid in such a manner that it forms a layer at the bottom of the vessel, we shall find that a violet colour will be produced at the contact-surface of the two liquids; the heat in this, as in the former case, being sufficient to cause the formation of nitrous acid. In searching, therefore, for small quantities of nitrates, it is advisable to add, as recommended by De Richemont, a large bulk of concentrated sulphuric acid. With respect to the delicacy of this test for nitrites, I have found that a liquid containing the $\frac{1}{8,000}$th part of nitrous acid (in the form of a soda-salt) becomes immediately coloured green upon the addition of a small quantity of sulphuric acid and sulphate of iron; that perceptible shades of green are produced when a liquid contains the $\frac{1}{500,000}$th, and a faint colorisation with the $\frac{1}{1,000,000}$th part. In like manner to the preceding test, I have found that a solution of pure nitrate of potassa which has been treated in the cold with concentrated sulphuric acid, or decomposed with tartaric acid, has no action whatever upon a solution of sulphate of indigo, but that the presence of the smallest quantity of nitrous acid is sufficient to destroy the same. By applying heat to the mixture of sulphuric acid

and solution of nitre, to which a few drops of indigo-solution have been added, the colour of the latter will be found rapidly to vanish, and the test then becomes an exceedingly delicate one for nitrates, and in the absence of chlorates and organic matter, may be most advantageously employed for them. I have examined the delicacy of the test for nitrites, and have found that the one, two and three millionth part of nitrous acid in a solution may be detected by means of it.

By all the foregoing tests it will be found that the sulphuric acid of commerce, as well as most kinds of carbonate of potassa, contain a trace of nitrous acid. In conclusion, I may state that I have applied the nitrites to the detection of the iodides, the results of which experiments will be found in the accompanying communication.

XIV.—*On a New Test for Iodides.*

By David S. Price, Ph.D., F.C.S.

Having in the preceding paper pointed out the principle on which the detection of nitrites by means of iodide of potassium and hydrochloric acid depends, I shall proceed briefly to describe the application of nitrites for the detection of iodides, and at the same time give one or two instances of the practical application of the test, in cases where the quantity of iodine is exceedingly small.

The method of employing the test is the following. The liquid suspected to contain an iodide is mixed with starch-paste and acidified with hydrochloric acid, a solution of nitrite of potassa is then added, when, if much iodine be present, a dark-blue colour will be instantly produced; if a very small quantity only, as for instance the two or three millionth part, then a few seconds elapse before the blue colour makes its appearance. In this manner, I have detected the $\frac{1}{4,000,000}$th part of iodine dissolved in water as iodide of potassium. It will be seen that the test admits of a degree of delicacy not attainable by any of the other methods for detecting iodides, as well as being at the same time free from the disadvantages to which they are more or less subject; as for instance, in the employment of chlorine, which unless added very carefully to a liquid containing a trace of an iodide only, is almost sure to afford a negative result, from the chlorine combining with the iodine, and so preventing its acting on the starch. The same error may also

arise by the use of nitric acid, should the suspected liquid contain a large amount of chlorides.

I will now detail the two cases in which I have applied this test, in the one for the purpose of detecting iodine in cod-liver oil, the object being to see how small a quantity of the oil would suffice; in the other for the purpose of detecting iodine in marine vegetation. One ounce of ordinary brown cod-liver oil was saponified by a concentrated solution of caustic potash, and then carbonised in an iron spoon over an open fire; the residue was removed into a covered porcelain crucible and strongly heated, so as effectually to destroy all organic matter, and when cold, was digested with a small quantity of water and thrown upon a filter; the filtrate being acidified with hydrochloric acid, was then mixed with starch-paste, and tested with nitrite of potassa, which almost immediately produced a pale plum colour.

Sea-water contains so small an amount of iodine, that it is exceedingly difficult to detect even a trace of it in the mother-liquor from several pounds of water. Minute as this quantity must be, it is nevertheless collected and assimilated by many marine plants, and the following experiment enables us to demonstrate its presence in their juices. If we take a thin transverse sectional slice of the stem of the *Fucus laminaria digitata*, moisten it with a little starch-paste and dilute hydrochloric acid, and examine it by the aid of the microscope, we shall, upon adding a drop of a solution of nitrite of potassa to the same, be able most distinctly to observe the formation of iodide of starch. The presence of an iodide may be shown in a still more marked manner, by suspending the stem of the same plant in a dry atmosphere, when the surface, after the lapse of some hours or days, will become covered with numerous transparent crystals, which on examination will be found to consist principally of chlorides, but at the same time to contain so much of an iodine-compound as to impart an intense blue colour to the test-mixture.

Many marine plants, when placed in a fresh state in contact with the test-mixture, impart an orange colour to it, owing to the liberation of bromine.

XV.—*Observations on the Teas of Commerce.*

By R. Warington, F.C.S.

In my previous communication to the Society on this subject, in February, 1844,* I endeavoured to show that there exist two distinct

* Memoirs and Proceedings of the Chemical Society, II, 73.

kinds of green tea, known in commerce as *glazed* and *unglazed;* that the former is coloured by the Chinese with a mixture of Prussian blue and gypsum, to which a yellow vegetable colouring matter is sometimes added, while the latter are merely dusted with a small quantity of gypsum; that in the specimen of the so-called Canton gunpowder, this glazing or facing is carried to the maximum. I also mentioned, that I had never met with a sample of green tea in which the blue tint was given by means of indigo. Since the publication of that paper, I have been in communication with several parties of great experience in this subject, from whom I have received much additional information, which, with several experimental points of interest that have come under my own immediate observation, will form the subject of the present paper.

The first point to which I wish to call the attention of the Society is, the question of the blue colouring matter used by the Chinese for colouring the green teas being Prussian blue, because some doubts have been thrown on this subject from various quarters. Mr. Bruce thus states:* "The Chinese call the former (the Indigo) *Youngtin,* the latter (the sulphate of lime) *Acco.*" Now I am favoured with the opinion of Mr. J. Reeves on this point, whose knowledge and experience render him most competent to decide in such a case; he believes that indigo is *never* employed for colouring used on tea, that the term Youngtin, as used by Mr. Bruce should be Yong-teen, *foreign blue,* the name given by the Chinese to Prussian blue in contra-distinction to Too-teen, *native blue, or indigo;* this, I think, is very conclusive evidence, and shows that Mr. Bruce's statement was erroneous.

In another quarter a surmise has also been published on this same point. Mr. Fortune, in his entertaining work† on China, says, speaking of the ingredients used in dying the Northern green teas for the foreign market, p. 201, "There is a vegetable dye, obtained from *Isatis Indigotica,* much used in the northern districts, and called Tein-ching, and it is not unlikely that it may be the substance which is employed;" again, at p. 307, "I am very much inclined to believe that this (the Tein-ching) is the dye used to colour the green teas which are manufactured in the north of China, for the English and American markets." This question, however, I think is now satisfactorily settled, and the experimental evidence I had adduced of the material being Prussian blue of a darker or paler tint, placed beyond a doubt by a positive demonstration; for Mr. Fortune has forwarded,

* Report on the Manufacture of Teas, &c., by C. A. Bruce, Aug. 16, 1839.
† Three Years' Wanderings in the Northern Provinces of China, by Robt. Fortune.

from the north of China, for the Industrial Exhibition, specimens of these materials, which from their appearance, there can be no hesitation in stating are fibrous gypsum (calcined), turmeric root, and Prussian blue; the latter of a bright pale tint, most likely from admixture with alumina or porcelain-clay, which admixture may account for the alumina and silica found as stated in my previous paper, and the presence of which was then attributed possibly to the employment of kaolin or agalmatolite.

Mr. J. R. Reeves, in a letter to my friend, Mr. Thompson, dated July 1, 1844, commenting on my paper, says: "Mr. Warington's experiments have led him to correct results as to the substances used, which I know to be Prussian blue, gypsum (fibrous), and turmeric; the second being sulphate of lime; and the last, the 'yellow, or orange-coloured vegetable substance,' which Mr. W. does not otherwise name. That the colouring is not intended as an adulteration, I feel quite sure. It is given to suit the capricious taste of the foreign buyers, *who judge of an article used as a drink by the eye instead of the palate.* You well know how little the London dealers, even now, like the yellowish appearance of uncoloured green tea. The Americans, a few years since, carried the dislike even further than the English, and therefore the Chinese merchant had scarcely a chance of selling his tea unless he gave it a 'face' that would suit *their fancy.* The small quantity of the colouring matter used, must preclude the idea of adulteration as a matter of profit." Mr. J. Reeves states, "that in the East India Company's time, gypsum and Prussian blue were sometimes used upon hyson teas, Tien Hing using the first on his pale, bright hyson; Lum Hing, the latter on his dark, bright leaf; but these were only in minute quantities just sufficient to produce an uniform face."

It is still a question of interest, which I before alluded to, whether the gypsum in its *calcined* state, is not used for the absorption of the last portions of moisture and allowing the tea the better to withstand the damp of the sea voyage. Through the kindness of Dr. Royle, I have received, since my last communication, a sample of green tea from the Kemaon district, in the Himalayas, which is quite free from any facing, as are also the green teas of Java, a large number of which I have had the opportunity of examining, and which are exceedingly clean and genuine in their appearance and characters.

ON BLACK AND GREEN TEAS.

Although the preparation of green and black tea from the respective

plants, the *Thea Viridis* and the *Thea Bohea*, has been warmly advocated by many botanists, yet it is now, I believe, pretty generally admitted by all parties, that both green and black teas can be and are made, indiscriminately from the same parcel of leaves, taken from the same species of plant. It is also well known to all persons, that the infusions from these teas, have marked differences of colour and of flavour, and that the effects produced on some constitutions by green tea, such as nervous irritability, sleeplessness, &c., are very distinct from those of black tea. Their characteristic physical differences are too well known to require any comment, but they have peculiar chemical properties to which we shall have occasion to allude more particularly presently, and which have always been attributed by chemists to the effect of high heat in the process of manufacture.

The question presents itself then—from whence do these distinguishing peculiarities arise, and to what are they to be attributed? From observations made in other directions, in the course of the routine work of the establishment to which I am attached, I had formed in my own mind certain conclusions on this subject. I allude to the exsiccation of medicinal herbs; these are for the most part nitrogenous plants, as the *Atropa belladonna*, the *Hyoscyamus niger*, the *Conium maculatum*, and others. The plants are brought to us by the growers or collectors from the country, tied up in bundles, and when they arrive fresh and cool they dry of a good *bright green* colour; but on the contrary, it is found that if they are delayed in their transit, or remain in a confined state for too long a period, they become heated, from a species of spontaneous fermentation, and when loosened and spread open emit vapours, and are sensibly warm to the hand; when such plants are dried, the whole of the *green colour* is found to have been destroyed, and a *red-brown* and sometimes a *blackish-brown result* is obtained. I had also noticed that a clear infusion of such leaves evaporated carefully to dryness was not *all* undissolved by *water*, but left a quantity of *brown oxidised extractive matter*, to which the denomination *Apothene* has been applied by some chemists; a similar result is obtained by the evaporation of an infusion of black tea. The same action takes place by the exposure of the infusions of many vegetable substances to the oxidising influence of the atmosphere; they become darkened on the surface, and this gradually spreads through the solution, and on evaporation the same *oxidised extractive matter* will remain insoluble in water. Again, I had found that the green teas, when wetted and re-dried, with exposure to the air, were nearly as dark in colour as the ordinary black teas. From these observations, therefore, I was

induced to believe that the peculiar characters and chemical differences which distinguish black tea from green, were to be attributed to a species of heating or fermentation, accompanied with oxidation by exposure to the air, and not to its being submitted to a higher temperature in the process of drying, as had been generally concluded. My opinion was partly confirmed by ascertaining from parties conversant with the Chinese manufacture, that the leaves for the black teas were always allowed to remain exposed to the air in mass, for some time before they were roasted. Mr. Ball, in his valuable work,* on the manufacture of tea, has described in detail the whole routine of these interesting processes, fully confirming my preconceived opinions, and of which I cannot do better than give you a summary. Some of the facts, I believe, had been published in Batavia in 1844, by Mr. Jacobson,† in the Dutch language. In the preface to his work, Mr. Ball says: "It will be seen by dates incidentally adverted to, that the facts and most of the materials of this work, were established and collected thirty years ago."—"These facts, as well as other materials, were derived from conversation with growers and manipulators from the tea districts; from written documents furnished by Chinese; from published works in the same language diligently sought out; and also from correspondence with a Spanish missionary long resident in the province of Fokim. These were all put into their present form full twenty years ago, and were read to one or two friends during my residence in China."—"They were not, however, so arranged, with any view to immediate publication."—"They were thus disposed as the best mode of recording and keeping together, the facts and materials I had collected."—"But it was not till the year 1844, when I received Mr. Jacobson's Handbook on the cultivation of tea in Java, that I found my own views so far confirmed, and my information such as to justify me in bringing my labours to a close."

The processes peculiar to the preparation of black tea, are styled Leang-Ching, To-Ching, and Oc-Ching, and these all consist in carefully watched and regulated processes of *spontaneous heating* or *slow fermentation* of the leaves until a certain degree of fragrance is developed. The leaves are said to *wither and give*, and become soft and placid. The utmost care, practical skill, and experience is required in the properly conducting these operations, and as soon as the proper point is arrived at, the leaves are to be immediately removed

* An Account of the Cultivation and Manufacture of Tea in China, by Saml. Ball, Esq.
† Handboek v. d. Kult. en Fabrik v. Thee.

to the Kuo or roasting-pan. After being roasted and rolled two or three times, they are then to be dried, and this is effected in the Poey-long, which consists of a cylinder of basket-work, open at both ends, and covered on the outside with paper; it is about 2½ feet in height and 1½ in diameter, which diameter is diminished in the centre like an ordinary dice-box to one foot and a quarter. This stands over and round a small charcoal fire, and is supplied with cross-bars about fourteen inches above the fire, on which an open sieve containing the tea is placed; and a small aperture about an inch and a half in diameter is made in the centre of the tea with the hand, so that an ascending current of air and the products of the combustion pass through and over the tea contained in the sieve. A circular, flat bamboo tray is placed partially over the mouth of this cylinder, and most probably serves to regulate the rapidity of the ascending current, prevent the admission of the cold air to the leaves, and at the same time allow a sufficient outlet for the generated watery vapours and the products of combustion. At the commencement of this operation, the moist leaves are still green and retain their vegetable appearance; after the drying has continued about half an hour, the leaves are turned, and again submitted to the heat for another half-hour; they are then taken out, rubbed and twisted, and after sifting away the small dust, again returned to the sieve and drying tube. This operation of sifting is very necessary, to remove any of the small tea or dust which might otherwise fall through the meshes of the sieve on to the fire, and the products of their combustion would deteriorate and spoil the flavour of the tea. The leaves have now begun to assume their black colour; the fire is diminished or deadened by ashes; and the operation of rolling, twisting, and sifting, is repeated once or twice until they have become quite black in colour, well twisted, and perfectly dry and crisp. They are then picked, winnowed, and placed in large quantities over a very slow fire for about two hours, the cylinder being closed.

Now, that this black colour is not owing to the fire is evident; for in cases mentioned by Mr. Ball, where the leaves have been dried in the sun, the same colour is obtained; and on the other side, if roasted first, without the process of fermentation or *withering*, and then finished in the Poey-long, a kind of green tea is produced.

In the operations for the manufacture of green tea, on the contrary, the freshly-picked leaves are roasted in the Kuo at once, without delay, at a high temperature; rolled and roasted again and again, assisted sometimes with a fanning operation to drive off the moisture; and always with brisk agitation until the drying is completed.

The marked differences in the mode of manufacture of black and green tea, will, I consider, after what has been stated, fully account for all the variation of physical and chemical properties to which I have before alluded.

ADULTERATION AND SOPHISTICATION OF TEAS.

Since writing my former paper, several teas have come under my notice, which must be classed under this head. The first I shall mention is a sophistication which has been carried on in this country to some extent, and consists in giving the appearance of green tea to an imported black tea. The material used as the bodies for this process of manufacture is a tea called scented caper; it is a small, closely-rolled black tea, about the size of small *gunpowder*, and when coloured, is vended under this latter denomination, the difference in price between the scented caper and this fictitious gunpowder being about 1*s.* per lb., a margin sufficient to induce the fraud. This manufacture has been carried on, I understand, at Manchester, and was kept as secret as possible; and it was only after considerable trouble that some of my friends succeeded in obtaining two different specimens for me, that could be fully depended on, as originating in this manufactory. It appears that it is generally mixed with other tea, so as to deceive the parties testing it. How this manufacture was conducted, I am not prepared to say; but some preparation of *copper* must have been employed, as the presence of that metal is readily detected in the specimens I received. I believe, however, that this sophistication has ceased.

I have now to call your attention to another adulteration of the most flagrant kind. Two samples of tea, a black and a green, were lately put into my hands by a merchant for examination, the results of which he has allowed me to make public. The black tea was styled *scented caper;* the green, *gunpowder;* and I understand they are usually imported into this country in small chests called catty packages. The appearance of these teas is remarkable; they are *apparently* exceedingly closely rolled, and very heavy; the reasons for which will be clearly demonstrated. They possess a very fragrant odour. The black tea is in compact granules, like shot of varying size, and presenting a fine glossy lustre of a *very black* hue. The green is also granular and compact, and presents a bright pale-bluish aspect, with a shade of green, and so highly glazed and faced, that the facing rises in clouds of dust when it is agitated or poured from one vessel to another; it even coats the vessels or paper on which it may be poured. On examining these samples, in the manner described in

my former paper, to remove this facing, I was struck by the tenacity with which it adhered to the surface, and which I had never remarked in any previous sample, requiring to be soaked for some time in the water before it could be detached; with this precaution, however, the greater part of the facing material was removed. It proved, in the case of the sample of green tea, to be a pale Prussian blue, a yellow vegetable colour, which we now know to be turmeric, and a very large proportion of sulphate of lime. The facing from the sample of black tea was *perfectly black* in colour, and on examination was found to consist of earthy graphite or black lead. It was observed, that during the prolonged soaking operation, to which these teas had been submitted, there was no tendency exhibited in either case to unroll or expand, for a reason which will be presently obvious. One of the samples was therefore treated with hot water, without however any portion of a leaf being rendered apparent. It increased in size slightly, was disintegrated, and then it was found that a large quantity of sand and dirt had subsided; this was separated by decantation, and collected; it was found to amount to 1·5 grains from 10 grains of the sample, or 15 in the 100 parts. It was evident, however, that much of the lighter particles must necessarily have been lost in the process of decantation; a weighed quantity of the sample was therefore carefully calcined, until the ash was quite white, and the whole of the carbonaceous matter burnt off, it yielded a result equivalent to 37·5 on the 100 parts. During this operation also, no expansion or uncurling of the leaf, as is generally to be observed when heat is applied to a genuine tea, was seen; in fact, it was quite evident that there was *no leaf to uncurl*, the whole of the *tea* being in the form of dust. The question next presented itself as to how these materials had been held together, and this was readily solved; for, on examining the infusion resulting from the original soaking of the sample, abundant evidence of gum was exhibited.

The sample of green tea was of a precisely similar kind to the black; it yielded 4·55 grains of ash, &c. from 10 grains of the specimen, or 45·5 per cent. A specimen of Java gunpowder yielded 5 per cent of ash; so that we have in this sample 40·5 per cent of dirt and sand over and above the weight of ash yielded by the incineration of a genuine tea.

Thus we have then in these samples a mixture of tea-dust with dirt and sand, agglutinated into a mass with a gummy matter, most probably manufactured from rice-flour, then formed into granules of the desired size, and lastly dried and coloured, according to the kind required by the manufacturer, either with black lead, if for black tea; or with Prussian blue, gypsum, or turmeric, if intended for green.

Since examining these two samples, I have obtained through a friend another specimen of green tea, having a very different appearance; that is, better manufactured, or rather, I should say, more likely to deceive the consumer, from its being made to imitate an *unglazed tea*. It is of a yellowish-green colour, scented and granulated as the former samples, and not much dusted; it yielded 34 per cent of ash, sand and dirt.

On inquiry, I have learnt that about 750,000 lbs. weight of these teas have been imported into this country within the last eighteen months, their introduction being quite of modern origin; and I understand that attempts have been made to get them passed through the Customs as *manufactured goods*, and not as teas; a title which they certainly richly merit, although it must be evident, from a moment's consideration, that the revenue would doubtless be defrauded, inasmuch as the consumer would have to buy them as teas from the dealer. It is to be feared, however, that a market for them is found elsewhere. The Chinese, it appears, will not sell them except as teas, and have the candour to specify them as *lie* teas; and if they are mixed with other teas of low quality, the Chinese merchant gives a certificate, stating the proportion of the *lie tea* present with the genuine leaf. This manufacture and mixing is evidently practised to meet the price of the English merchant. In the case of the above samples, the black is called by the Chinese, *lie flower caper;* the green, *lie gunpowder;* the average value is from 8*d*. to 1*s*. per lb. The brokers have adopted the curious term *gum and dust*, as applied to these lie teas or their mixtures, a cognomen which at first I had some difficulty in understanding, from the rapid manner in which the two first words were run together.

I may subjoin the results obtained from the careful incineration of a variety of teas, as they may be interesting, for the purpose of comparison, and illustrate the point I have mentioned as to these spurious teas being mixed with genuine ones.

Gunpowder tea, made in Java, gave 5·0 grains of ash in the 100 parts;

Gunpowder, during the East India Company's Charter	5·0
Kemaon hyson	6·5
Assam hyson	6·0
Lie gunpowder, No. 1	45·5
,, No. 2	34·0
Scented caper	5·5
Lie flower caper	37·5
Mixtures containing these lie teas, No. 1	22·5
,, ,, No. 2	11·0

XVI.—*On the Composition and Properties of the Carbonates of Lead constituting the White Lead of Commerce.*

By J. Arthur Phillips, F.C.S.

Having had occasion to devote considerable attention to the manufacture of commercial white lead by the old Dutch method, I have, in order to better understand the principles on which this process depends, been induced to undertake a numerous series of experiments on the physical and chemical properties of various specimens of this substance, prepared both by the ordinary process of slow corrosion, and also by precipitation from the salts of lead by the carbonated alkalies.

Many of the results obtained during these investigations being merely of a practical nature, and consequently of but little interest to the scientific chemist, have been omitted in the present paper, in which I shall chiefly confine myself to an examination of the composition of the carbonates of lead used as pigments, and of the several temperatures at which they undergo decomposition.

On referring to the analyses of this substance which have from time to time been published in the scientific journals, very considerable differences in the results obtained by the authors of the various papers cannot but be remarked. In some instances, also, no mention is made of the temperature to which the substance was exposed previous to analysis; but having been led to believe that this circumstance alone might be sufficient to account for many of the differences above referred to, I have in my own experiments paid especial attention to this subject.

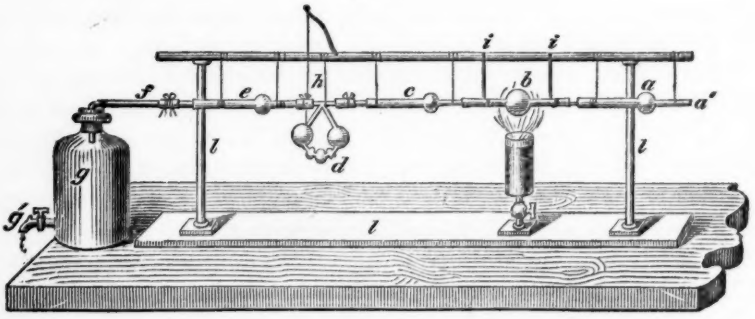
On subjecting portions of hard dry lead, fresh from the tan beds, to the desiccating influence of sulphuric acid under the exhausted receiver of an air pump, until they ceased to lose weight, I have invariably found that the loss sustained amounted to about 0·001 of the total quantity of the substance used.

If the salt which has been thus treated be taken from beneath the exhausted receiver, and afterwards exposed in a steam-bath for several successive days to a temperature of 212° Fahr., no further diminution of weight will in any case be found to occur; and as this temperature may even be increased to 220° without further affecting the weight of the salt operated on, I have assumed that the water which this substance retains, when so treated, is in chemical combination, and forms an essential ingredient of ordinary white lead.

In order to ascertain the exact composition of this compound, a known quantity was, after drying at 212° until it ceased to lose weight, introduced into a bulb blown in a tube of hard glass, through which a current of pure dry air was made to pass. This bulb was afterwards heated to redness for the purpose of expelling the carbonic acid and water, of which the former was collected and weighed in a Liebig's potash apparatus, and the latter in a chloride of calcium tube.

The accompanying figure will serve to explain the nature of the apparatus employed, and the different precautions taken to prevent error in the results obtained.

FIG. 1.



The tube *a*, which is firmly fitted by means of a perforated cork to the bulb-tube *b*, is filled with caustic potash broken into small pieces, and slightly plugged at its two extremities with pieces of cotton wool, to prevent any particles of potash from being mechanically drawn into *b*, and vitiating the results obtained. The other extremity of the tube *b*, which is of hard German glass, and in which the white lead to be analysed is placed, is connected by another perforated cork with the chloride of calcium tube *c*, which is itself united by a caoutchouc connector with the Liebig's apparatus *d*. To the potash bulbs succeeds a second chloride of calcium tube *e*, which is joined by connectors and a long glass tube *f*, to the aspirator *g*, by means of which a current of air may be readily drawn through the whole arrangement.

To make an analysis with this apparatus, the tube *b*, closed with two accurately-fitting corks, is first weighed when empty. A quantity of the substance to be examined is now introduced into the bulb, and the end being again closed with the corks before employed, the whole is re-weighed, and the difference between the two weighings evidently corresponds to the quantity of white lead which it contains. The

tube and its contents are then placed on two iron hooks *i i*, and the weights of the tubes *c* and *e* afterwards taken and noted, as well as those of the potash apparatus *d*, and the whole of the arrangement is put together and tied to the frame *l*, as shown in the figure.

The potash apparatus is now placed in an inclined position by means of the strings *h*, and by closing up the orifice *a'*, and at the same time turning the tap *g'*, the tightness of the various joints and corks is readily tested. Should the current of water, which at first issues from the tap, rapidly diminish in volume, and subsequently cease altogether, it shows the arrangement to be air-tight, and the experiment may be at once proceeded with.

For this purpose the opening *a'* is uncorked, and the tap *g'* so turned as to allow the water to escape in slow successive drops. The current of air which is thus drawn through the apparatus, will, in passing through the tube *a*, lose both its moisture and carbonic acid, and consequently arrive in the tube *b*, in a pure and perfectly dry state. The flame of a spirit-lamp, or gas jet, is now cautiously applied to the bulb, which is by slow degrees heated to bright redness.

A short time after the application of the flame, a certain amount of water is observed to pass into the tube *c*, and continues to do so until the substance becomes nearly red-hot. At the expiration of half an hour, the operation will be completed, and after being allowed to cool, the various tubes are closed with proper corks, and weighed. The excess of weight on the tubes *c* and *e*, and potash apparatus *d*, should exactly correspond to the loss sustained by *b*. The increase of weight on *c* represents the amount of water found, and that on the united weights on *d* and *e* the quantity of carbonic acid present.*

The following results were obtained by the analysis of different varieties of hard lead taken directly from the bed, and subsequently heated to 212° Fahr., until no further loss of weight was observed.

W. BLACKETT LEAD.

FIRST ANALYSIS.

Weight operated on = 32·94 grs.

Weight of carbonic acid found	= 3·71 grs.	=	11·26 p. c.
„ oxide of lead .	= 28·50 „	=	86·52 „
„ water . . .	= ·74 „	=	2·24 „
	32·95		100·02

* The employment of the tube *e* becomes necessary on account of the quantity of moisture carried off by the dry air from the potash apparatus. This in most instances amounted in my experiments to about 0·20 grs. in each operation.

SECOND ANALYSIS.

Weight operated on = 22·46 grs.

Weight of carbonic acid found	= 2·53 grs.	=	11·26 p. c.
„ oxide of lead .	= 19·43 „	=	86·51 „
„ water . . .	= ·50 „	=	2·23 „
	22·46		100·00

The above results may be thus expressed:

	I.	II.
Carbonate of lead . .	68·53	68·43
Oxide of lead . . .	29·23	29·34
Water	2·24	2·23
	100·00	100·00

DARLINGTON LEAD.

FIRST ANALYSIS.

Weight operated on = 15·26 grs.

Weight of carbonic acid found	= 1·79 grs.	=	11·73 p. c.
„ oxide of lead .	= 13·16 „	=	86·23 „
„ water . . .	= ·32 „	=	2·09 „
	15·27		100·05

SECOND ANALYSIS.

Weight operated on = 20·23 grs.

Weight of carbonic acid found	= 2·33 grs.	=	11·52 p. c.
„ oxide of lead .	= 17·50 „	=	86·50 „
„ water . .	= ·41 „	=	2·02 „
	20·24		100·04

Or,

	I.	II.
Carbonate of lead =	71·29	70·00
Oxide of lead . =	26·67	28·02
Water . . =	2·09	2·02
	100·05	100·04

The specimens of white lead, of which the composition is above given, were extremely hard and firm; but in some of the corrosions

by the Dutch process, a peculiarly soft, spongy variety is obtained, which crumbles under the touch, and has a remarkable effloresced appearance. This lead is much less dense than that ordinarily made, and the coating formed on the surface of the metal, is in most cases very superficial. The results obtained, are therefore considered unsatisfactory by the manufacturer; not only on account of the small percentage of white lead produced, but also because of its possessing less body than the other kinds. From the physical properties of this lead being different from those of common, well-prepared white lead, it was thought of interest, to examine whether its chemical constitution was the same as that of the harder kind; and with this view, the following specimens of soft lead were subjected to analysis.

W. BLACKETT LEAD.

FIRST ANALYSIS.

Weight operated on = 17·75 grs.

Weight of carbonic acid found	= 2·04 grs.	=	11·49 p. c.
„ oxide of lead .	= 15·29 „	=	86·14
„ water . . .	= ·42 „	=	2·37 „
	17·75		100·00

SECOND ANALYSIS.

Weight operated on = 20·64 grs.

Weight of carbonic acid found	= 2·41 grs.	=	11·67 p. c.
„ oxide of lead .	= 17·77 „	=	86·09 „
„ water . . .	= ·48 „	=	2·32 „
	20·66		100·08

Or,

	I.	II.
Carbonate of lead .	69·80	70·93
Oxide of lead . .	27·83	26·83
Water . . .	2·37	2·32
	100·00	100·08

DARLINGTON LEAD.

FIRST ANALYSIS.

Weight operated on = 19·70 grs.

Weight of carbonic acid found	= 2·24 grs.	=	11·37 p. c.
„ oxide of lead .	= 17·02 „	=	86·40 „
„ water . . .	= ·44 „	=	2·23 „
	19·70		100·00

SECOND ANALYSIS.

Weight operated on = 22·73 grs.

Weight of carbonic acid found	= 2·66 grs.	=	11·70 p c.
„ oxide of lead . .	= 19·58 „	=	86·14 „
„ water . . .	= ·50 „	=	2·20 „
	22·74		100·04

Or,

	I.	II.
Carbonate of lead . .	69·09	71·09
Oxide of lead . . .	28·68	26·75
Water	2·23	2·20
	100·00	100·04

The foregoing results indicate that each of the four different specimens examined, was composed of two equivalents of carbonate of lead, united to one equivalent of the hydrated oxide of that metal, and the composition of this salt will therefore be represented by the formula 2 PbO. CO_2 + PbO. HO.

The numbers given beneath, which represent the mean composition of the specimens analysed, and the theoretical percentages of a salt so constituted, will be found to agree very closely:

	Theoretical.	Mean of results obtained.
Oxide of lead	86·38	86·31
Carbonic acid	11·31	11·50
Water .	2·31	2·21
	100·00	100·02

Several other specimens of white lead were examined during the progress of these investigations; but in rare instances only did the results obtained indicate a formula differing from that above given.

An exceptional composition of this kind was observed in a specimen of Blackett lead, which was analysed by the method already described, and yielded the following numerical results:

FIRST ANALYSIS.

Weight operated on = 20·97 grs.

Weight of carbonic acid found	= 2·61 grs.	=	12·44 p. c.
„ oxide of lead .	= 17·96 „	=	85·69 „
„ water . .	= ·32 „	=	1·52 „
	20·89		99·65

SECOND ANALYSIS.

Weight operated on = 19·40 grs.

Weight of carbonic acid found	= 2·47 grs.	=	12·73 p. c.
„ oxide of lead .	= 16·56 „	=	85·36 „
„ water . .	= ·32 „	=	1·64 „
	19·35		99·73

Or,

	I.	II.
Carbonate of lead	75·63	77·37
Oxide of lead .	22·51	20·72
Water . .	1·52	1·64
	99·66	99·73

The composition of this specimen appears to correspond very closely with that of a salt, having the formula 3 PbO. CO_2 + PbO. HO, as will be observed on comparing the two columns of figures given beneath, of which one represents the mean results obtained by analysis, whilst the other shows the theoretical composition of a body having the above formula.

	Theoretical.	Mean of results obtained.
Oxide of lead .	85·66	85·52
Carbonic acid .	12·62	12·68
Water . . .	1·72	1·58
	100·00	99·78*

Another of the specimens of Darlington lead examined, afforded results which would indicate the composition expressed by the formula 5 PbO. CO_2 + PbO. HO.

* In no instance could any appreciable quantity of acetate be detected in the specimens of white lead examined.

From the great difference observed in the colour and body of various specimens of precipitated white lead, which were prepared by a variety of methods, during the progress of the practical investigation before referred to, it was thought desirable to examine the nature of the salts so produced, and also to determine the varying circumstances under which they are severally formed.

When an equivalent of pure carbonate of soda is dissolved in hot water, and continuously added to a hot solution of an equivalent of nitrate of lead, it will be observed that, on the introduction of the first drop of the soda-solution, a violent effervescence takes place. This is repeated on the addition of every fresh portion of the alkaline carbonate, until about two-thirds of it have been added, when carbonic acid ceases altogether to be evolved; although a white precipitate is still formed on the introduction of each additional quantity of the soda-salt.

If, on the contrary, the hot solution of nitrate of lead be added to that of carbonate of soda, no evolution of gas ensues until about two-thirds of the lead-salt have been introduced, at which point effervescence begins, and is continued in a greater or less degree until the whole of the liquor has been added.

Of the three specimens of precipitated carbonate of lead examined, and of which the composition is given beneath, the first was prepared by adding a small quantity of carbonate of soda, in solution in hot water, to a boiling solution of nitrate of lead in large excess. The second variety was obtained by adding the hot solution of carbonate to the dissolved lead-salt, until the mixture acquired an alkaline reaction. The third salt was produced by adding a solution of nitrate of lead to one of carbonate of soda, until the former was in slight excess. Both solutions were used hot.

The three precipitates thus obtained, were subsequently washed and dried at 212° Fahr. until they ceased to lose weight by further exposure at that temperature. On subjecting them to analysis, by the method before detailed, the following results were obtained:

PRECIPITATED LEAD, No. 1.

FIRST ANALYSIS.

Weight operated on = 22·72 grs.

Weight of carbonic acid found	=	3·28 grs.	=	14·43	p. c.
„ oxide of lead .	=	19·20 „	=	84·50	„
„ water . .	=	·25 „	=	1·10	„
		22·73		100·03	

SECOND ANALYSIS.

Weight operated on = 29·11 grs.

Weight of carbonic acid found	= 4·20 grs.	=	14·43 p. c.
„ oxide of lead .	= 24·59 „	=	84·47 „
„ water . .	= ·32 „	=	1·10 „
	29·11		100·00

Or,

	I.	II.
Carbonate of lead .	87·69	87·69
Oxide of lead . .	11·24	11·21
Water . . .	1·10	1·10
	100·03	100·00

PRECIPITATED LEAD, No. 2.

FIRST ANALYSIS.

Weight operated on = 32·84 grs.

Weight of carbonic acid found	= 5·12 grs.	=	15·59 p. c.
„ oxide of lead .	= 27·55 „	=	83·89 „
„ water . .	= ·21 „	=	·63 „
	32·88		100·11

SECOND ANALYSIS.

Weight operated on = 24·25 grs.

Weight of carbonic acid found	= 3·75 grs.	=	15·46 p. c.
„ oxide of lead .	= 20·37 „	=	84·00 „
„ water . .	= ·13 „	=	·54 „
	24·25		100·00

Or,

	I.	II.
Carbonate of lead . .	94·70	93·95
Oxide of lead . . .	4·78	5·51
Water	·63	·54
	100·11	100·00

PRECIPITATED LEAD, No. 3.

FIRST ANALYSIS.

Weight operated on = 25·74 grs.

Weight of carbonic acid found	= 4·18 grs.	=	16·23 p. c.
„ oxide of lead .	= 21·50 „	=	83·52 „
„ water . .	= ·08 „	=	·31 „
	25·76		100·06

SECOND ANALYSIS.

Weight operated on = 22·26 grs.

Weight of carbonic acid found	= 3·65 grs.	=	16·39 p. c.
„ oxide of lead .	= 18·58 „	=	83·46 „
„ water . .	= ·06 „	=	·27 „
	22·29		100·12

Or,

	I	II.
Carbonate of lead . .	98·63	99·60
Oxide of lead . .	1·12	·25
Water	·31	·27
	100·06	100·12

On examining the above numerical results, it will be observed that in neither case do the analytical numbers found lead to any rational formula, although it will be seen that in the two first products, the water and oxide of lead are present in very nearly equivalent proportions, and the precipitate may therefore be regarded as a mechanical mixture of carbonate and hydrate of oxide of lead. In the third analysis there is, however, an evident excess of water, probably arising from the substance not having been allowed to dry for a sufficient time before its introduction into the tube in which its decomposition was effected.

It was observed during the examination of the different varieties of white lead, that they all retain their hygrometric water with great obstinacy, as a continual loss of weight was in most instances found to occur during the first forty-eight hours after placing the substance in the water-bath; but as this loss is altogether far from considerable, it is probable that in the case of the third specimen of precipitated lead, the loss which occurred during the interval intervening between the two last weighings was so small that it was not perceived, and that

the substance was consequently analysed in a slightly damp state. The precipitated specimens were also found to be decomposed with much greater difficulty than those made by the ordinary process, and on this account, great care was required to prevent the melting of the tube in which the decomposition was affected.

On examining the ordinary corroded leads in a finely divided state, by the aid of a powerful microscope, no traces of crystalline structure could be perceived, even when the soft effloresced variety was employed; but when the three precipitate specimens were subjected to a power of 300 diameters, distinct hexagonal plates became visible. These varied from $\frac{1}{8000}$th to $\frac{1}{10000}$th of an inch in diameter, and appeared slightly yellow by transmitted light.

ANALYSIS OF A SPECIMEN OF NATIVE CARBONATE OF LEAD FROM TEESDALE, IN THE COUNTY OF DURHAM.

The carbonate selected for the purpose of analysis was in the form of imperfect opaque crystals, externally coated with a thin layer of hydrated oxide of iron. After carefully removing this covering with the edge of a sharp knife, and examining the surfaces of the crystal through a strongly magnifying lens, to determine if the whole had been scraped off, they were pulverised in an agate mortar, and after being dried at 212° Fahr., until they ceased to lose weight, were analysed by the method employed in the examination of the artificial carbonates. In this case, no water was remarked to pass from the decomposition-tube; and the perfectly anhydrous nature of the compound is evident from the following analytical results:

FIRST ANALYSIS.

Weight operated on = 33·03 grs.			
Weight of oxide of lead found	= 27·61 grs.	=	83.56 p. c.
„ carbonic acid .	= 5·30 „	=	16·05 „
	32·91		99·61

SECOND ANALYSIS.

Weight operated on = 25·11 grs.			
Weight of oxide of lead found	= 20·98 grs.	=	83·55 p. c.
„ carbonic acid .	= 4·15 „	=	16·52 „
	25·13		100·07

These numbers would of themselves indicate the presence of about 2 per cent of oxide of lead in the mineral examined; but on subjecting another portion of the same substance to the usual routine

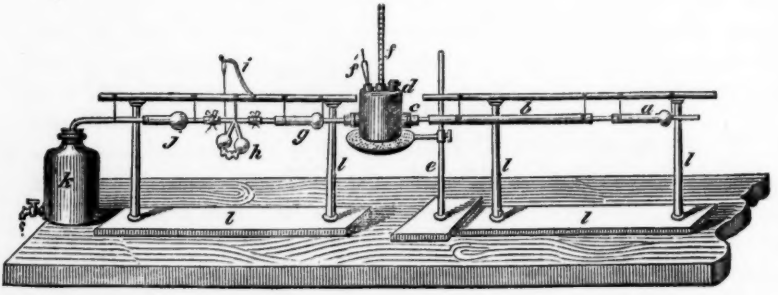
employed in chemical analysis, it was found to contain 1·23 per cent of siliceous matter, besides traces of iron and lime; and there can consequently be but little doubt that the crystals examined were composed of anhydrous carbonate of lead, slightly contaminated with earthy matter, and containing small portions of the carbonates of lime and protoxide of iron.

The results obtained during the foregoing experiments on the composition of white lead, made by the Dutch process, very nearly correspond with those of Mulder, who examined specimens which indicated compositions agreeing with the first two of the formulæ above given. Ch. Link* has also communicated an investigation of five different specimens of German white lead, all of which yielded results indicating the composition expressed by the formula 2 Pb O. CO_2 + PbO. HO.†

Dr. Richardson, of Newcastle-on-Tyne, who has examined this subject, has, however, obtained very different results from those found by Mulder, Link, and others, and I have therefore endeavoured to discover, if possible, the cause of this apparent discrepancy. The experiments made by this chemist were executed on specimens of white lead which had been heated for a certain time to the temperature of 300° Fahr. before being analysed. His percentages also indicate the total absence of water in the whole of the ten different specimens which he has examined.‡

From the high temperature at which Dr. Richardson's specimens were dried, it was thought probable that the water, and even traces of the carbonic acid present, might be expelled before the substance was subjected to analysis; and in order to determine this point I made use of the following apparatus.

FIG. 2.



* Ann. Ch. Pharm. XLVI, 232.

† Similar results have also been obtained by Hochstetter.

‡ Professor Graham's Elements of Chemistry, p. 591.

The tube *a* is filled with caustic potash coarsely powdered and connected by means of a smaller tube and perforated corks with the long piece of combustion-tube *b*, filled with fused chloride of calcium. The copper oil-bath *d*, is furnished with apertures through which are inserted the thermometer *f*, and the tube *f'* for the escape of the vapours generated. The sides of this vessel are also provided with tubulatures, so placed as to admit the tube *c c*, which is firmly held in its place by perforated corks. The apparatus connected on the other side of the oil-bath is the same as that employed to collect the water and carbonic acid in the former experiments, *g* and *j* being chloride of calcium tubes, and *h* a Liebig's potash apparatus, held in a slightly inclined position by the support *i*.

In order to use this arrangement, the bath is filled with oil to above the level of the tube *c c*, and placed on a sand-bath supported by the stand *E*. The weights of the tubes *g*, *h* and *j*, are now carefully taken and noted, and a weighed quantity of the white lead to be examined is placed in the tube *e e*. This is done by introducing the substance in a small porcelain trough, in which it had been previously heated until it had ceased to lose weight in the water-bath. The various parts of the apparatus are now connected, as shown in the figure, and suspended on the supports *l l*. When this has been done, the tap of the aspirator *K* is so far opened as to allow the water which it contains to escape in intermittent drops, and the sand-bath is heated by a small gas-burner protected from currents of air by a metal screen.

By operating in this way on numerous specimens of corroded lead, it was observed that the whole of the water was expelled by subjecting it during six hours to a temperature of 300° Fahr., and it was further found that the pulverised lead began to lose its water between 225° and 250° of the same scale.

During these experiments, no loss of carbonic acid had in any instance occurred at the temperature to which the salt was subjected, and further investigations were therefore made with a view of determining approximatively the point at which this elimination first takes place. With this view, the temperature was in the next experiment raised to 350°, and on re-weighing the various parts of the apparatus at the expiration of four hours, the substance was found to have lost traces only of carbonic acid.

On subjecting, however, 70·25 grains of carbonate of lead having the formula $2\ PbO.\ CO_2 + PbO.\ HO$ to a temperature of 400° Fahr. during ten consecutive hours, it was found to have lost 1·62 of water

and 1·65 of carbonic acid, and its percentage composition was consequently represented by the following numbers :

	Found.	Theoretical.
Oxide of lead .	90·60	91·06
Carbonic acid .	9·40	8·94
	100·00	100·00

On examining this result, it will be found that, besides the whole of the water, exactly one-fourth of the carbonic acid present had been expelled, and the salt remaining in the porcelain trough was consequently a dicarbonate of lead, having the formula $PbO.CO_2 + PbO$. This residue had not in the least altered in appearance from the time of its introduction into the oil-bath, being perfectly white, and exactly resembling ordinary white lead.

The above results were confirmed by numerous other experiments, but I have not yet determined at what temperature the second atom of carbonic acid is driven off.

From the foregoing experiments it is, however, evident that common white lead loses the whole of its combined water at 300° Fahr., and that at a temperature of about 50° higher, its carbonic acid begins also to be eliminated.

XVII.—*On the Combination of Arsenious Acid and Albumen, with Remarks on Liebig's Theory.*

By Sheridan Muspratt, Ph.D., F.R.S.E.

My time has been so much occupied, the last year, that I have had no opportunity of investigating, thoroughly, the compound of arsenious acid and albumen. I have latterly, however, paid considerable attention to this subject, owing to the following statement appearing in the Transactions of the Chemical Society :* "If water so readily extracts arsenious acid both from the compounds formed in the laboratory, and from those which nature has prepared, surely we may conclude that its retention is simply mechanical, and affords no ground for the theory which that eminent chemist, Liebig, has raised upon it."

* Chem. Soc. Qu. J. III, 16.

Liebig writes: "Arsenious acid enters into a very firm combination with membranes and gelatinous tissues; the arsenious acid combining with these, gives to them the power of resisting decay and putrefaction."

I cannot believe that so renowned a philosopher could have published such statements, unless he was convinced of their correctness from experiments and analysis. I now enter upon my researches.

QUALITATIVE ANALYSIS.

I took 0·107 grm. of dissolved arsenious acid and 12·67 grms. of the glairy albumen of eggs. They were intimately triturated together for about twenty minutes, coagulated by heat, and evaporated to dryness in a water-bath. The white residue, affused with distilled water and filtered, yielded a filtrate which gave *no deposit* of arsenic on copper by Reinsch's test, nor any stains on porcelain by Marsh's apparatus. When the residue on the filter was heated with pure sulphuric acid, and then submitted to the preceding experiments, arsenical indications were immediately obtained, proving that a combination of arsenious acid and albumen had occurred.

QUANTITATIVE ANALYSIS.

61·07 grms. of albumen were mixed as above with 0·603 grm. of dissolved arsenious acid, I washed the mixture, after evaporation to dryness, with distilled water, until not a trace of arsenious acid dissolved out.

The filtrate was introduced into a bottle provided with a glass stopper, some hydrochloric acid added, and a stream of sulphide of hydrogen passed through the menstruum. The flask was then closed, and allowed to rest for some hours; after this, pure carbonic acid was transmitted through its contents with the view of expelling all the free sulphide of hydrogen: the sulphide of arsenic was then collected on a tarred filter, dried at 100° C., and weighed.

Weight of tersulphide of arsenic . .	0·270
Equal to, of arsenious acid . . .	0·217

The above results, therefore, prove incontestably that the albumen had combined with 0·386 grm. of arsenious acid. This compound is not poisonous. I heard from Professor Gregory that he performed some experiments in Dublin in 1837, which satisfied him that Liebig was right; and Sir Robert Kane has stated that the "com-

pound of albumen with the acids is generally somewhat soluble; with metallic oxides insoluble."*

When the white of egg is used as the antidote to metallic poisons, it acts no doubt mechanically as well as chemically—a large portion being enveloped and protecting the mucus membrane of the stomach, while a small portion *enters into combination.*

The analytical results cited are to my mind so convincing, that to descant further upon the matter would be superfluous; and I may close this notice with the following able remarks of a medical man, with which I entirely coincide.

"There is in my opinion no doubt that the metallic poisons are capable of uniting with animal matters; and this I apprehend is perfectly well known to all toxocologists, and is the universally received explanation of their antiseptic properties."

XVIII.—*Examination of an Ore of Cinnabar, from New Almaden, California.*

By Adam Bealey, Esq., M.A.

This ore has long been known to mineralogists as abundant and very accessible, but it had not attracted much notice until the recent development of the mineral wealth of California led to more extended inquiry into the actual extent of its distribution, and rendered improved methods of reducing it, of great interest and value.

The mine, or principal deposit of this mineral, is thus described by Lyman in 1848:†

"New Almaden lies between San Francisco and Monterey, near the coast. It is 1200 feet above the plain, and is situated upon a ridge of the Sierra Azul, which consists of a greenish talc-rock.

"The cinnabar is found in nests, in a stratum of a yellowish earth, which is 42 feet in thickness. The occurrence of this mineral has been known to the natives from time immemorial, as the cave of red earth, which they employed for painting their bodies.

"During Lyman's stay, the daily produce from 1,600 lbs. of cinnabar, distilled in a rudely constructed apparatus, was from 200

* Chemistry of Agriculture and Physiology, page 377.

† Liebig and Kopp's Annual Report, by Hofmann and De La Rue. Vol. II, p. 388.

to 300 lbs. of mercury, and in the last three weeks of his residence, the total amount of mercury obtained was about 10,000 lbs.

"Cinnabar had likewise been found in fifteen or twenty other places, within a circumference of a few miles."

A more recent account of this mine was politely communicated by Dr. Forbes, and accompanied a specimen of the ore sent to Professor Hofmann for analysis, at whose suggestion the following examination was undertaken.

"The mine of New Almaden is situated in Upper California, near Santa Clara, on the coast, not far from San Francisco. It is the property of a company of English and foreign merchants, and is leased to a company of the same kind.

"It has been in active operation for about six or eight months. The vein is very large, and 'crops out' on the surface, where it is worked. The metal is extracted from the ore in two ways:

"First, by a series of large iron cylinder-retorts, heated in furnaces, and discharging their produce into water, where the metal is condensed.

"Secondly, by brick furnaces, in which the fuel (wood) is intermixed with the ore. By these operations, the ore gives from 30 to 45 per cent of its weight of mercury.

"The mine produced in the month of November, 1850, not less than 127,500 lbs. of mercury."

The ore as exhibited in the specimens sent, some of which weighed as much as 14 avoirdupoise lbs., has a bright red colour, slightly inclining to purple, and appears to have been imperfectly cleared from a soft, light-brown earth, which can easily be scraped from its surface. It breaks without much difficulty under the hammer, and is afterwards easily reduced to powder, with the exception of some bright crystalline particles, which are extremely hard.

The surfaces of recently broken ore appear much more purple than those long exposed. It is traversed at irregular intervals by very thin bands of white, hard, crystalline material, apparently calcareous and siliceous. When in the state of fine powder, it has a very brilliant vermillion colour, many shades darker than the massive ore. Its sp. gr. is 4·410.

In a preliminary examination, it exhibited the ordinary phenomena of a mercurial sulphide associated with siliceous matter. A portion of the ore was digested with nitro-hydrochloric acid, and the insoluble residue separated by filtration.

The solution examined by the usual methods contained mercury, sulphur, iron, alumina, a trace of nickel, lime and magnesia.

The part insoluble in acid consisted of silicic acid, and very minute traces of lime and potassa.

In estimating the principal constituents of this ore, the mercury was determined as sulphide of mercury, and as metallic mercury by distillation with lime.

1. 2·238 grms. gave 1·801 grm. of sulphide of mercury.
2. 1·057 „ „ 0·860 „ „
3. 250 grms. distilled with 500 grms. of lime, gave 175·540 grms. of metallic mercury.

The sulphur was estimated as sulphuric acid.

1. 1·349 grm. gave 1·120 grm. of sulphate of baryta.
2. 1·248 „ „ 1·025 „ „

Iron as sesquioxide.

1. 1·940 grm. gave 0·024 grm. of sesquioxide of iron.
2. 1·610 „ „ 0·022 „ „

Lime as carbonate of lime.

1·940 grm. gave 0·0485 grm. of carbonate of lime.

Alumina.

1·940 grm. gave 0·012 grm. of sesquioxide of aluminum.

Magnesia as pyrophosphate of magnesia.

1·940 grm. gave 0·0525 grm. of pyrophosphate of magnesia.

Insoluble residue.

1. 1·349 grm. of ore gave 0·193 grm. of silicic acid.
2. 2·238 „ „ 0·325 grm. of silicic acid, and traces of lime and potassa too slight to be estimated.

The percentages corresponding to these numbers will be found in the table appended at the end of this note.

CINNABAR FROM ALMADEN, SPAIN.

As the appearance of an ore of cinnabar so rich in mercury, and found in such profuse abundance, seems likely to have a material influence upon the permanent supply ordinarily found in commerce, a comparison was instituted between this and the ore derived from Almaden, in Spain, well known as the chief source of Spanish mercury.

The specimen of ore examined was obtained from Mr. Tennant,

and described as one from which a considerable part of Spanish mercury was derived. It is like the Californian ore, massive, but much less brilliant and much harder. Throughout its mass, small patches of yellow iron pyrites are irregularly distributed. When in the state of fine powder, it has a dull, brick-red colour, in striking contrast with the brilliant vermillion cinnabar from California. Its sp. gr. is 3·622.

Submitted to the same examination, and treated similarly to the last, it exhibited the same phenomena, with variations too slight to require especial notice.

The part soluble in acid consisted chiefly of mercury, sulphur, iron, with traces of alumina and lime; the part insoluble in acid, of silicic acid and alumina.

The principal constituents of the mineral were determined as before: Mercury as sulphide of mercury; iron as sesquioxide of iron; sulphur as sulphuric acid; silicic acid as such.

Mercury.

1. 1·009 grm. of ore gave 0·443 grm. of sulphide of mercury.
2. 1·0205 „ „ 0·447 „ „

Sulphur as sulphuric acid.

1·0205 grm. of ore gave 1·208 grm. of sulphate of baryta.

Iron.

1·009 grm. gave 0·148 grm. of sesquioxide of iron.

Insoluble residue.

1. 1·0205 grm. gave 0·357 grm. of silicic acid and alumina.
2. 1·009 „ „ 0·353 „ „

I have moreover examined specimens of cinnabar ore from Moschellandsberg and from Wolfstein.

CINNABAR FROM MOSCHELLANDSBERG.

This specimen and the following one were obtained from Mr. Griffin, and described as being worked, though of comparatively rare occurrence.

The mineral is a dark, red-brown crystalline material, heavy, very hard, and with difficulty reduced to powder. Its sp. gr. is 4·735

Examined and treated as the minerals previously mentioned, it was found to consist principally of mercury, sulphur, iron, alumina

and silicic acid. Mercury and sulphur only were determined quantitatively.

Mercury.

1. 1·166 grm. of ore gave 0·902 grm. of sulphide of mercury.
2. 1·255 „ „ 0·967 „ „

Sulphur as sulphuric acid.

1·3075 grm. gave 1·050 grm. of sulphate of baryta.

Insoluble residue.

1·3075 grm. gave 0·2235 grm.

CINNABAR FROM WOLFSTEIN.

This ore is a grey, earthy-looking mineral, with dark livid patches occurring at intervals in its substance. It is very hard, and becomes a light puce-coloured powder. It was found to consist of mercury, sulphur, alumina and a trace of iron, and silicic acid.

1·516 grm. yielded 0·316 grm. of sulphide of mercury.

From the above results the following per centages were calculated:

COMPOSITIONS OF VARIOUS CINNABAR ORES.

	CALIFORNIAN.				ALMADEN, SPAIN.			MOSCHELLANDSBERG.			WOLFSTEIN.
	1.	2.	3.	Mean.	1.	2	Mean.	1.	2.	Mean.	
Mercury .	69·36	70·13	70·23	69·90	37·84	37·75	37·79	66·60	67·13	66·86	18·00
Sulphur .	11·38	11·21	—	11·29	16·22	—	16·22	11·01	—	11·43	
								Insol.			
Iron . .	1·23	—	—	1·23	10·36	—	10·36	residue 17·09	—	17·09	73·31
Lime . .	1·40	—	—	1·40							
Alumina .	0·61	—	—	0·61							
Magnesia .	0·49	—	—	0·49							
					Silicic acid and						
Silicic acid	14·30	14·52	—	14·41	alumina . .		35·12				
				99·33			99·49				

From these numbers it is evident that, provided the specimens represent the average minerals worked, the ore of California contains nearly double the amount of mercury found in the Almaden ore, and nearly fourfold that of the specimen of Wolfstein, while it approaches the composition of pure cinnabar, even more nearly than the mineral of Moschellandsberg.

XIX.—*A Simple Aspirator.*

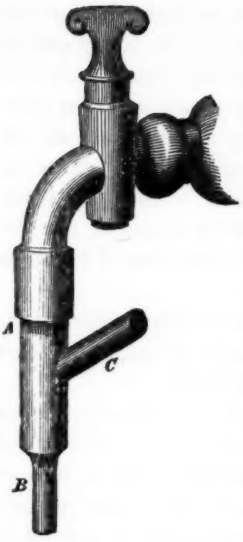
By Matthew W. Johnson, Esq.

The contrivance usually adopted in the laboratory for establishing a current of air, is a large vessel filled with water, which, flowing out, is replaced by an equal volume of air. An apparatus of this kind is attended with some inconvenience from the large space it occupies, and the necessity of continually supplying water, which requires the frequent intervention of the operator.

Being engaged (during the autumn of 1848) in some experiments where a constant stream of atmospheric air was requisite, a simple arrangement suggested itself to me, by which these evils are obviated.

This arrangement is based upon the well-known suctional power exerted by a jet of water issuing under certain pressure from a comparatively narrow orifice, a fact which is described and elucidated in all manuals of physics. This suctional power may be easily illustrated experimentally by inserting the horizontal limb of a glass tube, bent at a right angle, at a short distance from the orifice, into the vertical tube from which the water escapes; if the aperture of the vertical limb of the tube be introduced into a vessel of water, the latter will be lifted to a greater or smaller height in it, and, under certain circumstances, actually flow out with the main jet. It is evident that the same force which lifts the water, may also be used for creating a current of air, and that, in this manner, the common cock of any waterpipe may perform the office of an aspirator.

The apparatus which I have the honour of laying before the Society, is extremely simple. It consists of a small tube of brass, glass, or caoutchouc, open at both ends and provided at *C* with a somewhat narrower tube, as represented in the annexed sketch



The size of the aspirator must vary to a certain extent with that of the water-cock. I found the following dimensions: *A* 2 inches by $\frac{3}{8}$ths of an inch; *B*, 1 by $\frac{3}{8}$ths; *C*, 1 by $\frac{3}{8}$ths, convenient for adaptation to the ordinary water-cocks in the laboratory of the Royal College of Chemistry (of which the diameters are $\frac{3}{8}$ths of an inch).*

The opening *A* is connected by a vulcanised India-rubber tube with the water tap; *B*, in the same manner, with a glass tube, the length of which varies according to the force of the current to be established; the tube *C* is finally attached to the vessel through which the air is to be drawn. If now the water be turned on, not fully (for the water rushing with full force into the tube would escape both from the lower and the lateral opening), but partially, a very uniform and abundant current of air is drawn in at *C* and divided into single bubbles, which are carried down with the water through the lower opening.

I have made a few experiments with this apparatus, which I will mention, as they may serve to illustrate its action.

On applying the aspirator to water-cocks in three separate rooms, each room about 20 feet above the other, with a view to ascertain whether increased pressure above the cock caused air to be sucked in with increased force, the effect was found to be the same in each case. On the other hand, the length of tubing attached to the lower opening *B*, exerted a marked influence on the force of the current. Several trials showed that air can be forced through a column of water one-fourth the height of the lower tube of the aspirator, continuously, and with sufficient rapidity for ordinary purposes.

This holds good for moderate lengths of tubing; on very consi-

* The elegant contrivance arranged by Mr. Johnson, the satisfactory working of which in the laboratory I can testify from personal experience, depends upon the well-known principle of the *Wassertrommel (trombe hydraulique)*, a blasting machine, not so frequently employed at present as formerly, but used even now in Germany and France, when trifling pressures only are required. The air is drawn in by the suspended suction-column, and is to a certain extent proportional to its length.

The adaptation of this principle to the purposes of the laboratory is likely to meet with more general approbation than has been bestowed upon its use in practice on a large scale.—A. W. H.

derably increasing the length of the lower tube, a slight diminution of this proportion was observed. On attaching to the lower end of the aspirator a tube about 25 feet long, and connecting the lateral opening with a vessel containing mercury, into which an open tube dipped, I found that a constant and sufficiently rapid stream of air was drawn through a mercurial column, $5\frac{1}{2}$ inches high. Now $5\frac{1}{2}$ inches of mercury correspond to 5 feet of water. The long tube, however, was not absolutely tight, which probably accounts for the slight deficiency of power, as air ought to have been forced through quite 6 feet of water, under the circumstances.

The following trial was made in order to obtain some information regarding the velocity with which air is aspired by means of this instrument, and likewise the amount of water wasted.

A tube 8 inches long, and $\frac{1}{8}$ths of an inch in diameter, being attached to the lower end of the aspirator, allowed of $50\frac{1}{2}$ cubic inches of air being passed through in 53 seconds, with a loss of 35·19 cubic inches of water. This is the mean of three experiments. According to this, 1 cubic inch of air requires about 1 second of time, and 0·69 cubic inch of water is lost. With the ordinary aspirator, the amount of water expended equals the amount of air aspired; but by employing this new apparatus, 31 per cent of water is saved. It is evident that the width of the lower tube must influence these data to a certain extent; but as in all laboratory apparatus compactness is much more important than a slight saving of time, or a trifling reduction in cost, I have not examined this question more minutely.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

April 7, 1851.*

CHARLES DAUBENY, M.D., F.R.S., President, in the Chair.

Thomas Spencer, Esq., was elected a Fellow of the Society.

The following presents were announced:

Picket (M.A.) "Essay on Fire," Translated from the French. London, 1791.

Priestly (Joseph, LL.D.) "Heads of Lectures on a course of Experimental Philosophy, particularly including Chemistry," delivered at the new College in Hackney.

"Nicholson's Journal of Natural Philosophy and Chemistry," Vol. VII, 8vo. London, 1804.

Watson (R., D.D) "A plan of a course of Chemical Lectures," 8vo. Cambridge, 1771.

Watson (R., D.D.) "An Essay on the Subjects of Chemistry, and their general division," 8vo. Cambridge, 1771.

Babington (William, M.D.) and William Allen, F.L.S. "A Syllabus of a course of Chemical Lectures read at Guy's Hospital," 8vo. London, 1802.

* The minutes of the Anniversary Meeting, held on March the 31st, together with the President's and Treasurer's Reports, will be given in the following number. The President's Report was in the possession of the late Mr. Richard Phillips at the time of his decease, and has not yet been found.

Martine (George, M.D.) "Essays and Observations on the Construction and Graduation of Thermometers, and on the Heating and Cooling of Bodies," 12mo. Edinburgh, 1787.

"Vocabulary and Tables of the Old and New Nomenclatures," (Anonymous).

Brisson (J. M.) "Elements of the Natural History and Chemical Analysis of Mineral Substances." Translated from the French, 8vo. London, 1800.

Lagrange (J. B. Bouillon). "A Manual of a Course of Chemistry." Translated from the French, 2 vols. 8vo. London, 1800.

Gren (F. A. C.) "Systematisches Handbuch der gesammten Chemie." Erster und zweiter Theilen, 8vo. Halle, 1794.

Macquer (M.) "Elements of the Theory and Practice of Chemistry," 2 vols. 8vo. London, 1764.

Lavoisier (M.) "Essays, Physical and Chemical." Translated from the French, by Thomas Henry, F.R.S., 8vo. London, 1776.

Presented by P. J. Chabot, Esq., M.A.

"Journal de Pharmacie et de Chimie," Tome I—IV, 1842—3.

"Repertoire de Chimie," Tome I—V, 1837—8.

Thénard (L. J.) "Traité de Chimie," Tome I, II. Bruxelles, 1830.

Raspail (F. V.) "Nouveau Système de Chimie Organique," Tome I, II. Bruxelles, 1830.

Presented by Robert Warington, Esq.

"The Proceedings of the American Philosophical Society," Nos. 4 and 5: by the Society.

"The Pharmaceutical Journal for April:" by the Editor.

"The Philosophical Transactions, and the Proceedings of the Royal Society of London:" by the Society.

The following papers were read:

1. "On the Composition of the Water of the Dee and Don at Aberdeen, with an Investigation into the action of Dee Water on Lead Pipes and Cisterns," by John Smith, M.D., Fordyce Lecturer on Agriculture, and Assistant in the Chemical Laboratory of Marischal College.

2. "On a peculiar property of Ether and some Essential Oils," by Dr. C. F. Schönbein.

April 21, 1851.

The President, in the Chair.

William Liddeard, Esq., was elected a Fellow of the Society.

The following papers were read:

1. "Analysis of Sediment deposited from the River Nile in Lower Egypt:" by Matthew W. Johnson, Esq., Student in the Royal College of Chemistry.
2. "Notice of a Specimen of Chlorobromide of Silver, from Chili:" by Colonel Philip Yorke.

May 5, 1851.

The President, in the Chair.

The following presents were announced:

Priestley (Joseph, LL.D.) "Experiments and Observations on different kinds of Air, and other Branches of Natural Philosophy," 3 vols.: by William Odling, Esq.

"Reports of the Friday Evening Meetings of the Royal Institution for March:" by the Institution.

Daubeny (Charles, M.D.) "Brief Remarks on the Correlation of the Natural Sciences:" by the Author.

Daubeny (Charles, M.D.) "A Tabular View of Volcanic Phenomena, comprising a List of the Burning Mountains that have been noticed at any time since the commencement of Historical Records, or which appear to have existed at antecedent periods, together with the dates of their respective Eruptions, and of the principal Earthquakes connected with them:" by the Author.

"Chapman (Professor) on the fundamental relations of Mineralogy to Chemistry and Physics, and on the general study of the Science:" by the Author.

"The Journal of the Franklin Institute for March:" by the Institute.

"The Pharmaceutical Journal for May:" by the Editor.

The following papers were read:

1. "On the Tests for Nitrates, and a new one for Nitrites:" by David S. Price, Ph.D.
2. "On a new Test for Iodides:" by David S. Price, Ph.D.
3. "Analysis of Milk:" by John Ellis Roberts, Esq.

May 19, 1851.

ROBERT PORRETT, Esq., Vice-President, in the Chair.

Daniel Stone, Esq., was elected a Fellow of the Society.

The following papers were read:

1. "Observations on the Teas of Commerce:" by Robert Warington, Esq.
2. "On the Composition and Properties of Carbonates of Lead, constituting the White Lead of Commerce:" by J. Arthur Phillips, Esq.
3. "Mr. Matthew W. Johnson exhibited and described a new and simple form of Aspirator.

June 2, 1851.

The President in the Chair.

Neville S. Maskelyne, Esq., and George Whipple, Esq., were elected Fellows of the Society.

The following presents were announced:

"A Specimen of Kreatine:" by Dr. Gregory.
"The Pharmaceutical Journal for June:" by the Editor.
"Silliman's American Journal for March and May:" by the Editors.
"The Reports of the Meetings of the Royal Institution for April and May."

The following papers were read:

1. "On the Equivalent of Phosphorus:" by Professor A. Schrötter.
2. "Notes on a Cause of Leakage in a Leaden Water-cistern:" by J. H. Gilbert, Ph.D.
3. "On Dibenzoylamide, a new Derivative of Oil of Bitter Almonds:" by Joshua H. Robson, Esq., Student in the Royal College of Chemistry.

June 16, 1851.

Robert Warington, Esq., Vice-President, in the Chair.

The following papers were read:

1. "On Chromic Acid and Sesquioxide of Manganese:" by Adam J. Fainie, Esq.
2. "On the Chromate of Ammonia:" by the same.
3. "On Etherification:" by Professor Williamson.
4. "On the Valuation and Composition of Protochloride of Tin:" by Professor Penny.
5. "On the Chemical Examination of the Metals and Alloys known to the Ancients:" by J. Arthur Phillips, Esq.

NOTICES

OF

PAPERS CONTAINED IN THE

"Philosophical Transactions" and Foreign Journals.

On the Condition of certain Elements at the moment of Chemical Change.

By B. C. Brodie, F.R.S.*

(ABSTRACTED BY THE AUTHOR.)

The experimental inquiry contained in the present paper is so intimately connected with certain theoretical considerations in which it took its rise, that it has not appeared desirable to separate it from them. Indeed, to its right comprehension, it is necessary to be placed at the point of view from which it was conceived. The general object of the paper may be considered as to prove that, at the moment of chemical change, the same chemical relation exists between the particles of which certain elements consist, as between the particles of compound substances under similar circumstances, on which relation the phenomena of combination and decomposition depend; that, in short (to use the common language), the particles of the element have a chemical affinity for each other. This term affinity, however, is not appropriate to express the relation which exists between the particles of a decomposing substance, and I would substitute for this the term "polar relation," which is applicable to the condition of the particles of the decomposing as well as of the composing body, and also indicates an analogous condition, which I conceive to exist, between a series of particles undergoing chemical change, and a series of particles conducting electricity or magnetism.

In the case of a decomposing body, the proof of this polarisation of its particles is of a very subtle nature, and lies in the fact, that, at the moment of change, they exhibit certain peculiar phenomena of combination, of which this hypothesis renders a rational account. The existence of these phenomena is a well-known fact, and has been not altogether incorrectly stated in common language, which attri-

* Phil. Trans. II, 1850, 759.

butes, and with a certain truth, peculiar combining properties to nascent bodies. I shall here confine my remarks on this subject to one or two experiments, which may briefly show, in the case of compound substances, the kind of phenomena to which I shall show the parallel in the case of the elements. Silver (for example), cannot be oxidized by the direct action of oxygen on the metal, but oxide of silver is readily formed by boiling chloride of silver with potash. The particles of oxygen and silver have, therefore, acquired, by their combination with the chlorine and potassium, a chemical relation or affinity which the (so-called) isolated elements have not. Oxygen that is associated with potassium has very different combining properties to oxygen associated with other particles of oxygen. This is the fact. The rational conception of this change is given in the expression

$$\overset{+}{\underset{\smile}{\mathrm{Ag}}}\ \overset{-}{\mathrm{Cl}}\ \overset{+}{\mathrm{K}}\ \overset{-}{\underset{\smile}{\mathrm{O}}} = \mathrm{AgO} + \mathrm{K\,Cl},$$

in which I have indicated the polar relation of the particles. In cases, on the other hand, where this polar division of the substances cannot take place, there is no chemical action. Thus, in the change which is thus represented:

$$\overset{+}{\mathrm{H}}\mathrm{SO_4}\overset{+}{\mathrm{K}}\mathrm{O} = \mathrm{SO_4K} + \mathrm{HO},$$

the two combinations which take place, are not two combinations accidentally simultaneous, but correlative and mutually dependent phenomena, which we cannot separate: for we know as a fact, that anhydrous sulphuric acid may be distilled off carbonate of potash, without alteration, there being in this case no tendency to that polar division which is necessary to the chemical change. These are phenomena of double decomposition, in which each of the substances which enter into the change is combined; but it does not appear that this state of combination is necessary to the action, but rather that peculiar chemical relation of the particles which is antecedent to combination. Thus, for example, when iodine and phosphorus decompose water in the usual mode of the formation of hydriodic acid. This decomposition is not simply due to the fact, that the iodine takes the hydrogen and the phosphorus the oxygen of the water, which breaks up, being acted upon by two opposite forces, but the chemical relation between the iodine and phosphorus is as essential and important a condition of the change as their relation to the water itself. The same remark applies to the decomposition of water by the joint action of chlorine and nitric oxide, which can be effected by neither substance alone. From the consideration that if this law were true at all, it must be universal, I was led to consider in what way chemical change

took place in the case of the elemental bodies. For the formation of these "uncombined particles," as they are considered by Berzelius, would be a fact of an altogether different order to the formation of a compound substance, and of which the very existence was a strange and unaccountable anomaly; for the decomposition and synthesis of a chemical substance are very different facts, regarded as a consequence of the peculiar mode of propagation of chemical change, or simply as the result of the binary, or other constitution of the body.

On reflection, examples occurred to me, both of the chemical division and chemical synthesis of the element in which various phenomena hitherto obscure found their explanation. The experiments of the first class show that a division of the elemental bodies, which occurs in certain cases of chemical change, is truly a chemical and not simply a mechanical division of the substance. This is shown by the fact that the particles of the element thus separated show the peculiar combining properties of "*nascent bodies.*" It is not necessary to my argument that the precise view which I have given of the nature of this nascent state (namely, that it is a polar state), should be taken, provided only it be allowed that these properties, in some way or other, depend on the fact that the particle is issuing from a state of combination, which is generally admitted.

1. The much-debated problem of the cause of the formation of sulphuric acid in the ordinary mode of its preparation, by the joint action of sulphurous acid and nitric oxide upon oxygen is a case in point. The oxidation of sulphurous acid under these circumstances is a proof of the chemical division of the oxygen; the one particle of oxygen being, so to say, *nascent* from the other, thus:

$$\underbrace{\overset{+}{N}O_2\,O\overset{-}{O}\,\overset{+}{S}O_2\overset{-}{}}=NO_3+SO_3.$$

This hypothesis explains the relation and interdependence of the two combinations which take place.

2. A yet more striking instance is given in the remarkable experiment by which Regnault* prepared chloro-sulphuric acid. Olefiant gas, as usually prepared from alcohol and sulphuric acid, contains a large quantity of sulphurous acid. When chlorine is brought in contact with this mixture of gases, two substances are formed, chloro-sulphuric acid and the Dutchman's liquid. Upon sulphurous acid alone (in the circumstances under which the experiment is made), chlorine has no action whatever, nor, according to Regnault, upon olefiant gas, when both gases are dry and only in diffused daylight. These combinations, therefore, are strictly an interdependent, the change being effected thus:

* Ann Ch. Phys. [2], LXIX, 176; and LXXI, 445.

$$\underbrace{\overset{+}{C_2}\,H_2\,\overset{-}{Cl}\overset{+}{Cl}\,\overset{-}{SO_2}} = C_2\,H_2\,Cl + Cl\,SO_2.$$

The chlorine in this case is divided exactly as the oxygen in the former experiment,—this division being comparable to the decomposition of a compound substance, as for example, to that already referred to, of water under the joint action of nitric oxide and chlorine which takes place thus:

$$\underbrace{\overset{+}{NO_2}\,\overset{-}{O}\,\overset{+}{H}\,\overset{-}{Cl}} = NO_3 + ClH.$$

The same reason which explains the oxidation of nitric oxide in this experiment accounts also for the combination of the chlorine and sulphurous acid in the other case.

3. When hydrogen and an oxide of nitrogen are passed together over heated platinum, the oxide of nitrogen is decomposed and ammonia and water formed. This experiment is strictly a case of double decomposition, both substances dividing and their elements mutually replacing each other, thus:

$$\left(\begin{matrix}\overset{+}{N}\,\overset{-}{O_3} \\ \overset{-}{H}\,\overset{+}{H_3}\end{matrix}\right) = NH_3 + 3\,HO,$$

4. Again, zinc, it is known, decomposes slowly and with evolution of hydrogen, a strong solution of caustic potash; but when into the solution a few crystals of nitre or nitrite of potash are thrown, the zinc is rapidly dissolved, with the evolution of ammonia. The reason of this I consider to be that the polar division of the zinc now takes place with greater facility, the metal being oxidized in two directions, and chemically divided exactly as the hydrogen in the last experiment, thus:

$$\underbrace{\overset{+}{H_3}\,\overset{-}{O_3}\,\overset{+}{Zn_3}\,\overset{-}{Zn_3}\,\overset{+}{O_3}\,\overset{-}{N}} = NH_3 + 6\,Zn\,O.$$

There are other examples of the same class, to which also are to be referred the phenomena of substitution. When one particle of chlorine combines with the hydrogen of an organic body, another particle of chlorine is thrown into an opposite chemical condition, and therefore rendered capable of combining with the remaining elements of the same, exactly as in the case of the formation of the chloro-sulphuric acid; so that a positive hydrogen is truly replaced by a positive chlorine, the particles being, thus far, in an identical chemical condition.

If these experiments be truly, as here asserted, evidence of the chemical division of the elements, the correlative fact, namely, their

chemical synthesis, must take place at their formation. Theory indicates this; and although the more usual mode of forming these bodies is not such as to bring to light the true nature of this process, there are other instances which disclose it.

1. For example, when an acid is added to a perfectly pure solution of an alkaline iodide, such as can readily be procured by precipitating any iodate it contains by baryta-water and filtering, the solution remains perfectly clear. Neither when an acid is added to a pure solution of iodate of potash, is there any alteration; but on mixing these solutions, an abundant precipitate of iodine is formed. The hydriodic and iodic acids decompose one another thus:

$$IO_6H + 5\,HI = 6\,HO + I_6,$$

the element being formed by the synthesis of particles from the two substances. To this synthesis of iodine, the division of that element, which takes place at the formation of the hydriodic and iodic acids, is the corresponding fact, to explain which we must assume the same polar difference between its particles.

2. In the course of his researches on the hypophosphites, Wurtz* discovered a very singular substance, the hydruret of copper. This body is formed by the action of hypophosphorous acid upon sulphate of copper. The analyses of Wurtz closely correspond with the formula Cu_2H, the change by which it is formed being simply a substitution of oxygen for hydrogen in one of the lower acids of phosphorus; as for example thus:

$$\underset{\text{(Phosphorous acid.)}}{PO_5H_2} + Cu_2O = PO_6H + Cu_2H.$$

In contact with strong hydrochloric acid, this body gives the following remarkable reaction. Hydrogen is evolved, and protochloride of copper, Cu_2Cl, formed. Both substances are decomposed, and the hydrogen evolved is exactly the double of that due to the simple decomposition of the substance. Hydrochloric acid does not act upon copper, and the presence of the hydrogen, on received ideas (as Wurtz remarks), "far from favouring this reaction, should add to it a new obstacle." This, on the other hand, is the simple result of the principles I have laid down. The decomposition is perfectly similar to that of the suboxide of copper under analogous circumstances, arises from the same cause, and may be expressed thus:

$$\underbrace{\overset{+}{Cu_2}\,\overset{-}{H}\,\overset{+}{H}\overset{-}{Cl}} = Cu_2Cl + H_2.$$

* Ann. Ch. Phys. [3], XI, 251.

The particles of hydrogen here combine, as do the hydrogen and oxygen in the other experiment:

$$\underbrace{\overset{+}{Cu_2}\,O\,H\overset{-}{Cl}}=Cu_2\,Cl+HO.$$

If this be not admitted, what, I will ask, is the reason for the atomic relation which exists between the decomposing bodies? The decomposition by water of the remarkable bodies discovered by Frankland, zinc-ethyl and zinc-methyl, is a perfectly similar case. Thus:

$$\underbrace{\overset{+}{Zn}\,\overset{-}{C_4\,H_5}\,\overset{+}{H}\,\overset{-}{O}}_{\text{(Zinc-Ethyl.)}}=ZnO\quad+\quad\underbrace{C_4\,H_5\,H}_{\text{(Hydride of Ethyl.)}},$$

the hydrocarbon taking the place of hydrogen in the other reaction. I have myself since realized the experiment in which both atoms of hydrogen are replaced by hydrocarbon thus:

$$\underbrace{Zn\,C_4\,H_5\,C_4\,H_5\,I}=ZnI+(C_4\,H_5)_2,$$

and shown the perfect analogy which exists between the action of hydrogen* and of the hydrocarbon, which is its analogue.

3. The formation of nitrogen by the decomposition of nitrite of ammonia, is a similar fact; it is an interchange of elements, which may be considered to take place within the substance thus:

$$\underbrace{\overset{+}{N}O_4\,H_4\,\overset{-}{N}}=4\,HO+N_2;$$

4. When a solution of bichromate of potash is poured into a strong and acid solution of the peroxide of barium in hydrochloric or nitric acid, a violent effervescence and escape of oxygen takes place. Apart, these solutions are perfectly stable; together, they are both decomposed. The chromic acid passes into chloride of chrome, the peroxide of hydrogen into water, and the oxygen formed is due to the simultaneous decomposition of both bodies.

$$3\,Cl\,H+2\,Cr\,O_3+3\,HO_2=Cr_2\,Cl_3+6\,HO+6\,O_2.$$

I regard the oxygen itself in this experiment as the true reducing agent, and I believe that the one particle of oxygen removes the other from combination, in the same sense, and for the same reason, as

* Chem. Soc. Qu. J. III, 406.

would a particle of hydrogen, were zinc thrown into the acid solution, the groupe HOO replacing the groupe Zn OH in the decomposition.

The decomposition of nitrite of ammonia by heat, which I have classed with these other experiments, is an instance of what is commonly called spontaneous decomposition. The transition is easy from this experiment to other cases, in which no one of the substances, usually called compound, but the elements alone, are formed; and, to be consistent, it must be admitted that in the very simplest case of decomposition, such as that of the chloride of nitrogen, or of the oxide of silver, by heat, the elements are not, as is generally supposed, simply eliminated from combination, but are formed by a chemical synthesis, the one particle of the substance decomposing the next; as for example, thus:

$$\underset{\text{Ag O O Ag}}{\underbrace{\overset{-}{\text{Ag}}\ \overset{+}{\text{O}}\ \overset{-}{\text{O}}\ \overset{+}{\text{Ag}}}} = \text{Ag}_2 + \text{O}_2.$$

This, at least, appears to me to be the logical inference from the experiments I have cited; for I cannot imagine that the formation of the element is in the one case a chemical synthesis, and in the other a fact of some totally different nature. It is more rational to conceive it, as in all cases, one and the same event.

From the development of these general views, I proceed to an experimental research, founded on them.

The discoverer of the peroxide of hydrogen, Thénard, observed some very singular properties of this body. To prepare the pure substances according to Thénard's direction, is a very tedious process; but the properties in question may all be observed with the neutral or alkaline solution of the peroxide of barium, in hydrochloric or acetic acid. Certain substances, such, for example, as finely divided platinum or carbon, decompose this solution with the evolution of oxygen. This decomposition is effected in the manner termed by Berzelius, catalytic, the substances themselves undergoing no alteration. There are, however, other bodies which cause this decomposition with yet greater energy, and themselves undergo a chemical change of the most surprising nature. These bodies are all those metallic oxides, which can readily be reduced; the oxides of gold, silver, and mercury, and the peroxides of lead, manganese, nickel, and other similar substances. These bodies decompose the solution, as does platinum or carbon, while the substances themselves also lose oxygen, and are reduced either to metal or a lower degree of oxidation. Chemical science has proved inadequate to explain the cause of these decompositions, which, indeed, are generally considered to be almost without parallel.

Considered, however, in connection with the experiments I have

just cited, and from the theoretical point of view of this paper, these facts come before us in a new light. Hitherto in the breaking up of the oxide of silver and the peroxide of hydrogen, no fact has been recognised but the simultaneous decomposition of two chemical substances; this is that for which it has been so difficult to account. Were it, for example, a hydride of silver which was thus decomposed by the peroxide, and the decomposition of the substances attended with the formation of water, the experiment would have attracted no attention. On the view here given, the formation of the oxygen is as truly a chemical synthesis as the formation of water itself, and may be substituted for it in a chemical change. This supplies an explanation of these facts, at once adequate and simple. The oxide of silver is here reduced by the oxygen of the peroxide of hydrogen, just as in other cases it might be by hydrogen itself, the formation of the silver being the corresponding fact in the decomposition of the oxide of silver, to the formation of water in the peroxide of hydrogen, so that the change may be represented thus:

$$\overset{+}{\underset{\smile}{\mathrm{H}}}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{O}}\overset{-}{\mathrm{Ag}}\tfrac{1}{2}\overset{+}{\mathrm{Ag}}\tfrac{1}{2}\overset{-}{\smile} = \mathrm{HO} + \mathrm{O}_2 + \mathrm{Ag}.$$

If this be the true representation of the nature of this decomposition, an atomic relation must exist between the particles of oxygen which thus combine; and in the existence of such an atomic relation would be found the truth of the hypothesis. I therefore applied myself to the determination of the quantitative relation which existed between the decomposing bodies, a point on which, as yet, no experiment existed.

In some preliminary experiments, I ascertained that the decompositions which take place with the peroxide of hydrogen, can also be effected with the peroxides of the alkaline metals. Thus, on placing peroxide of potassium, the substance, that is, produced by the action of potassium upon melted nitre, in contact with moist chloride of silver, I found that the chloride was reduced, with as much facility as by zinc, and oxygen evolved; and on extending my experiments to the peroxide of barium itself, I found that the same decomposition, and indeed all those which could be effected by the peroxide of hydrogen, took place with this substance, and with equal facility. Such explanations, therefore, of these experiments, as depended on the peculiarly unstable nature of the peroxide of hydrogen, at once fall to the ground. From the greater convenience for my purposes which the peroxide of barium afforded, I used it exclusively in the following experiments.

The peroxide of barium was prepared by passing dry oxygen gas over baryta, broken up into small pieces, and placed in a combustion-

tube, which was heated in the ordinary charcoal trough. The substance prepared in this manner, even with a very pure baryta, never contains the absolute theoretical amount of oxygen; and the object being the comparison of the loss of oxygen by the peroxide, to that lost by the silver compound reduced, it was necessary to find a means of readily determining the amount of oxygen contained in the different preparations. The method used was the determination of the weight of oxygen evolved by a known weight of the peroxide of barium dissolved in an acid, and decomposed by platinum. This was effected in a small apparatus, consisting of a flask with a tube attached to it, very similar to those often used for the determination of carbonic acid.

A verification of this method of determining the oxygen was made by weighing, in a tube, baryta before and after the absorption of oxygen, and then determining the amount of oxygen in the manner described. An experiment conducted in this way gave an increase of weight corresponding to 6·81 per cent of oxygen. The loss with platinum and hydrochloric acid gave 6·63 and 6·60 per cent. In pulverising the substance, it is impossible to prevent the absorption of a small quantity of water, which satisfactorily accounts for the slight difference between these two results.

In a similar manner, the amount of oxygen was determined which was evolved by the action of bichromate of potash and hydrochloric acid upon the peroxide of barium; and it was found that when a great excess of the bichromate was used, the bichromate lost 3, and the peroxide 4, equivalents of oxygen, that is, that the total loss of oxygen was to the loss from the peroxide as 7 : 4. When, however, smaller quantities of the bichromate are used, the result is very different. I at first used this reaction as a method of determining the oxygen in the substance, but subsequently abandoned it, as, for this reason, open to objection.

The method of weighing the loss of oxygen, which succeeds very well in the preceding experiments, cannot be used with advantage for determining the amount of oxygen given off by a metallic oxide in contact with the peroxide of barium. The evolution of gas is slow, continuing often for several days, and a larger quantity of water is required for the experiment than can conveniently be weighed. I was, therefore, obliged to determine indirectly the oxygen given off, by determining the amount of reduced metal.

The experiment is very simple. The weighed peroxide was intimately mixed in a flask with the metallic oxide, and a certain portion of water, about 12 ounces, poured upon the mixture. The action was allowed to continue until all evolution of gas had ceased. In the experiments with oxide and chloride of silver, the residue was treated with dilute hydrochloric acid, with which it was allowed to remain in contact at least twelve hours. All oxide was thus converted into

chloride. The fluid was now filtered from the residue, and the hydrochloric acid washed out. This residue was then extracted by boiling with dilute nitric acid, and the silver thus dissolved (being in fact the silver reduced), was estimated as chloride. This was the measure of the oxygen lost.

The experiments were made at 100° C. and at the temperature of the air; and are classified both with reference to the nature of the compound reduced, and also the particular preparation of the peroxide employed, both which circumstances affected them.

The results of each series of experiments are given in three tables, of which the first table (A) contains the numerical details of the experiments. In the second (B), the oxygen equivalent to the reduced silver is compared with the oxygen in the peroxide, the peroxide being taken as 100. In the third table (C), the oxygen lost by the peroxide is itself assumed as the unit. It is advisable to make both of these comparisons. I will extract certain of the tables, A and C, which will give a general idea of their nature.

*Experiments with Chloride of Silver.**—The following experiments were made with chloride of silver at 100° C:

TABLE I.—A.

	Peroxide of barium P.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	3·0115	0·527	0·280	0·0155
2.	3·014	1·003	0·3945	0·0219
3.	3·0865	1·404	0·5633	0·0312
4.	3·0455	2·057	0·8085	0·0449
5.	3·0036	4·011	1·019	0·0566
6.	3·0206	5·963	1·0573	0·0587
7.	3·0295	7·983	1·1815	0·0656
8.	2·958	9·235	1·087	0·0605
9.	2·967	11·139	1·170	0·0652
10.	3·0465	11·064	1·3105	0·0728
11.	3·0375	15·960	1·3515	0·0759
12.	3·0695	19·920	1·3425	0·0745
13.	3·0125	8·059	1·4795	0·0822

* The experiments are, in all the tables, arranged according to the amount of reduction, and not with reference to the quantity of the substances employed. But for the sake of a ready general comparison, nearly the same quantity of the peroxide, about 3 grms., was with some few exceptions employed. A sufficiently exact comparison can thus be made at a glance.

TABLE I.—C.

	Oxygen in the peroxide of barium = a.	Oxygen equivalent to the chloride of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		6·11		
2.		8·63		
3.		12·11		
4.		17·62		
5.		22·54		
6.		23·26	9 : 2	22·22
7.	100	26·13		
8.		24·46	4 : 1	25·0
9.		26 25		
10.		29·01		
11.		29·61	7 : 2	28·57
12.		29·01		
13.		32·73	3 : 1	33·33

In the first four of these experiments, in which comparatively small quantities of the chloride of silver, at most not half an equivalent, were taken, the loss increases nearly with the mass of the chloride, and bears, therefore, no constant ratio to the loss from the peroxide. In all four experiments the chloride has been reduced in nearly the same proportion; but yet between the first and second experiments there is a difference not found between the other three, as may be seen from the following comparison:

Exp.	Chloride of silver taken.	Chloride of silver found.
1.	100	53·1
2.	100	39·3
3.	100	40·1
4.	100	39·3

This gradual increase of loss with the mass of the chloride does not continue, or becomes very small; for one and three equivalents of chloride give nearly the same amount of reduction, equivalent to exactly $\frac{1}{4}$th of the oxygen in the peroxide. This loss can be increased to $\frac{3}{7}$ths. But here a point is reached, where, at any rate, a very great increase of the proportion of chloride taken causes no sensible alteration in the action.

The next tables contain experiments with chloride of silver at the temperature of the air:

TABLE III.—A.

	Peroxide of barium Q.	Chloride of silver taken.	Chloride of silver obtained.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	3·034	4·0125	1·366	0·076
2.	2·9942	4·988	1·480	0·0825
3.	3·0275	6·1315	1·545	0·08613
4.	2·994	8·0905	1·9415	0·10823
5.	2·9742	10·016	2·043	0·1138
6.	2·9532	14·916	2·019	0·1125
7.	3·014	9·9915	2·336	0·1302
8.	2·9915	12·9075	2·3125	0·1289
9.	2·0132	14·916	1·5485	0·0863

TABLE III.—C.

	Oxygen in the peroxide of barium Q = a.	Oxygen equivalent to the chloride of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		29·13	7 : 2	28·57
2.		32·05		
3.		33·10	3 : 1	33·33
4.		42·07	7 : 3	42·85
5.	100	44·52		
6.		44·28	9 : 4	44·44
7.		50·23		
8.		50·11	2 : 1	50·0
9.		49·88		

It will be observed that at this lower temperature a very great increase of reduction takes place. The comparative experiments in this and the last series, show that from corresponding quantities of the chloride, as nearly as possible twice the amount of silver is reduced, so that the expression of the relative loss of oxygen from the two substances, extend the series of ratios from 7 : 2 to 2 : 1, this last ratio forming a similar limit in this table to that of the ratio 7 : 2 in the preceding.

Experiments with Oxide of Silver.—The following experiments were made with oxide of silver at 100° C.:

TABLE V.—A.

	Peroxide of barium P.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	3·0225	0·855	0·625	0·0347
2.	3·0295	1·525	0·8353	0·0463
3.	2·9807	1·205	0·9784	0·0543
4.	3·006	1·832	1·165	0·0647
5.	3·0107	2·235	1·369	0·0760
6.	2·997	2·920	1·5565	0·0864
7.	2·982	4·692	1·492	0·0831
8.	3·007	4·890	1·510	0·0841
9.	3·0185	6·182	1·483	0·08238
10.	3·601	6·266	1·874	0·1041
11.	2·986	6·4675	1·503	0·0837
12.	3·067	9·339	1·6345	0·0908
13.	3·019	11·051	1·7325	0·09625
14.	3·0485	7·810	1·7785	0·0988
15.	2·983	4·932	1·84	0·1025
16.	3·616	15·675	2·395	0·133
17.	2·9725	9·5345	2·001	0·1115
18.	3·0075	12·2035	2·2365	0·1248

TABLE V.—C.

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		13·66		
2.		18·22	5 : 1	20·0
3.		21·82		
4.		25·77	4 : 1	25·0
5.		30·21	7 : 2	28·57

TABLE V.—C. (*continued*)

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
6.		34·53		
7.		33·33		
8.		33·45		
9.		32·61	3 : 1	33·33
10.	100	34·53		
11.		33·57		
12.		35·49		
13.		38·12		
14.		38·84	5 : 2	40·00
15.		41·12		
16.		44·00	9 : 4	44·44
17.		44·84		
18.		49·63	2 : 1	50·00

These experiments give similar results to those made with the chloride of silver at the lower temperature, and comprise a series of ratios beginning with 7 : 2 and ending with 2 : 1.

The following experiments were made also with oxide of silver, but at the temperature of the air:

TABLE VII.—A.

	Peroxide of barium P.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	2·999	0·824	0·528	0·2293
2.	3·004	1·605	0·9135	0·05075
3.	3·017	3·121	1·3915	0·0773
4.	3·022	3·994	1·6815	0·0934
5.	3·039	6·313	1·990	0·1105
6.	3·04	7·788	2·057	0·1142
7.	3·029	9·400	2·041	0·1133
8.	2·9417	2·964	2·2055	0·1225
9.	3·059	15·720	2·3785	0·132
10.	15·925	26·522	13·677	0·759
11.	3·478	9·405	2·965	0·1647
12.	3·021	7·6195	3·222	0·1796

TABLE VII.—C.

	Oxygen in the peroxide of barium P = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.		11·63		
2.		20·14		
3.		30·69	7 : 2	28·57
4.		37·17	5 : 2	40·0
5.		43·52		
6.	100	44·96	9 : 4	44·44
7.		44·84		
8.		49·88		
9.		51·67	2 : 1	50·00
10.		57·07		
11.		56·35	7 : 4	57·1
12.		71·22	7 : 5	71·42

The results are of the same general nature as before, but show a far greater amount of reduction. This loss may be increased yet further; for example, in two experiments made with another preparation, with a comparatively small quantity of the oxide of silver, the limit of the last table was at once reached.

TABLE VIII.—A.

	Peroxide of barium O.	Oxide of silver.	Chloride found.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	2·926	5·186	2·8557	0·1586
2.	3·06	5·064	3·0402	0·1682

TABLE VIII.—C.

	Oxygen in the peroxide of barium O = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.	100	71·59	7 : 5	71·42
2.		72·78		

In two other experiments this limit was exceeded.

TABLE IX.—A.

	Peroxide of barium Q.	Oxide of silver.	Chloride of silver found.	Equivalent of oxygen.
	grms.	grms.	grms.	grms.
1.	2·985	7·878	3·843	0·2142
2.	2·9544	7·9215	3·801	0·2119

TABLE IX.—C.

	Oxygen in the peroxide of barium Q = a.	Oxygen of the oxide of silver reduced = ψ.	Ratio, $a : \psi$.	Calculated ratio.
1.	100	83·56	6 : 5	83·33
2.		83·56		

This is the greatest amount of loss which I have yet obtained in these experiments with silver-compounds, which has never quite equalled the oxygen in the peroxide.

The specific difference in the amount of reduction of the chloride and oxide of silver under otherwise similar circumstances, that is with the same preparation of the peroxide and at the same temperature, rendered it an interesting matter of inquiry whether the same difference would be found with other silver-compounds. In four experiments made with carbonate of silver at 100°, and at the lower temperature, the result was nearly the same as with the chloride. But with sulphate of silver it was very different. In an experiment at 100°, with one equivalent of the sulphate, the loss from the peroxide to the loss from the sulphate was in the ratio of 40 : 1, the amount of reduction being so small, that the action of the sulphate of silver very nearly approached the so-called contact-action of platinum. The action of very small quantities of the chloride and oxide is also of the same nature. The action, therefore, of these different chemical substances only differs in degree; it approaches the same limit, but according to a different law.

I would willingly have attempted to render these series of experiments more complete, had it not appeared to me that there were certain defects in the method of experimenting which would render this attempt useless. One most important question is, whether the series of ratios, by which I have expressed the relative loss of oxygen from the two substances, is truly an intermittent or a continuous series, that is to say, whether there are or are not certain points where this ratio is constant, although the proportions of the masses and the temperature may be varied. That there is for each chemical

substance at least one such point, namely,* a certain limit of reduction, beyond which a great increase of the mass of the substance reduced does not alter the action, may, I think, be asserted with confidence, and, without in any way implying that all the ratios which these experiments have brought to light are of this nature; it seems to me very difficult to account for the great coincidence of experiments made with very different proportions of the substances, without admitting a tendency of the action to fall into certain ratios rather than into others; indeed, the experiments appear to me to indicate, both that, for certain intervals, the loss of oxygen truly does vary directly with the mass to be reduced, and that in certain other points the mass may be varied and the loss yet be constant. The experiments however are not sufficiently exact absolutely to decide this point. I may thus sum up the results of these experiments: 1st. The amount of oxygen lost by the substance reduced, is, under circumstances, otherwise similar, in a definite and constant ratio to the quantity of the peroxide of barium employed. 2nd. This loss is greater as the mass of the substance reduced is increased, and diminishes as the temperature at which the reduction takes place is raised. It varies also with the preparation of the peroxide. 3rdly. In each series of experiments, there is a certain definite limit of reduction, beyond which, at any rate, a very great increase of the mass of the substance reduced causes no increase of the loss of the oxygen. Lastly, in reference to that chemical question from which this inquiry proceeded, namely, how much oxygen is lost by the substance reduced in proportion to the loss from the peroxide of barium, it is to be observed, that, however much the circumstances are varied, there are yet two limiting ratios, between which the whole action is comprised, either of which may be very closely approached. These are the limits of least reduction, in which the ratio of the loss from the peroxide of barium to that from the metallic oxide is infinite, or as 1 : 0, and the limit of greatest reduction, the ratio of equality, in which the two substances would lose an equal amount of oxygen. This limit also, in no one experiment with any silver compound have I ever exceeded or reached. The first limit is that in which the action would be a pure reduction by contact, such as takes place when platinum or carbon are the substances which cause decomposition. The other would be a purely chemical action, such as may be seen in an experiment to which I will now proceed, and which

* It appears from other experiments which I have made, that with each chemical substance there is a specific limit of reduction of this kind. Thus, for example, in the experiment with chromic acid, the only reason of the constant reaction there obtained is that by taking a great excess of the bichromate I at once determined the action at a limit which it could not exceed. When similar quantites of the bichromate are employed the result is very different.

although not at first sight as striking as the reduction of the metallic oxides, is, philosophically considered, quite as remarkable, being indeed the same experiment, but detached from circumstances, which give, in the other cases, the apparent differences to the reaction.

Action of Iodine on the Peroxide of Barium.—It occurred to me that if it were for the reasons I have given, that the iodide and chloride of silver decompose the peroxide of barium, iodine and chlorine should produce a similar effect. Indeed, this was a very critical experiment; for we know the action of iodine on baryta, and on the view usually taken of this and of other analogous changes, namely, that the iodine takes away the barium from the oxygen because of its superior affinity for the metal, and that the oxygen thus liberated combines with the iodine because it is in a nascent condition, by acting on iodine with the peroxide of barium, we ought to have just twice as much iodic acid formed as in the other case. Nor on this view can I see any apparent reason why the oxygen from the peroxide should not effect this oxydation as would the oxygen from the baryta. On the other hand, from the theoretical considerations here given, another result might be anticipated. The condition for this combination of iodine and oxygen would be no longer realised. The oxygen, it is true, would be in a certain sense nascent, but it would be no longer in the same polar relation to the iodine. The reaction in the case of baryta may be thus expressed:

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Experiment gave this reaction. When water is formed upon a mixture of peroxide of barium and iodine, a violent evolution of oxygen takes place, and the same when chlorine is led into water containing the peroxide, or when the peroxide is thrown into a solution of hypochlorite of lime in acetic acid. In the experiment with iodine, the whole oxygen of the substance is evolved and not a trace of iodic acid formed. A mean of 10 experiments gave the ratio of the loss from the peroxide by the action of platinum and hydrochloric acid, to that evolved by the action of iodine as 100 : 198·4. I have also ascertained that with a perfectly pure peroxide, 1 equiv. of iodine decomposes exactly 1 equiv. of the peroxide, any excess of the peroxide remaining undecomposed. In this point, the reaction differs from the previous experiments with oxide of silver, in which very small quantities of the substance decompose in all cases the whole of the peroxide present.

The experiment with iodine may be presented from a point of view in which its absolute identity with the decomposition of the metallic oxides is at once seen. Iodine and water have many of the properties of a metallic peroxide; and it is reasonable to consider that the oxygen here formed, is formed by the synthesis of the particles of oxygen from the water and from the peroxide of barium, the water itself being reduced, thus:

$$\underset{\smile\!\!\!

different modes of action, and the relative velocity with which the two modes of decomposition take place. If, for example, the ratio of the loss of oxygen from the peroxide of barium to that from the metallic oxide be 4 : 1, three parts of the peroxide will have been decomposed by the contact and one by the chemical action; if the ratio be 2 : 1, it will have taken place in equal proportion between the two. With this view all the phenomena are consistent. As a fact, we know that the contact action proceeds more rapidly at a high than at a low temperature; we need not, therefore, be surprised if the relative velocity of this to the chemical action increases with the temperature. By increasing the mass of the oxide or chloride, on the other hand, the proportion of the chemical action is increased, and in this case we have a great reduction. This explains both the variation of the action and the constancy of the limits between which it is confined.

On the Action of Nitric Acid on various Vegetables, with a more particular examination of Spartium Scoparium.

By John Stenhouse, F.R.S.*

This paper is a continuation of a series of investigations intended to elucidate the nature of vegetables by means of chemical reagents. A preceding paper† contained an account of the action of sulphuric and hydrochloric acid on the *matière incrustante* of several plants belonging to different classes of the vegetable kingdom. The present paper contains an account of the action of nitric acid on various plants, the researches having been undertaken in the hope that, by means of this powerful reagent, some light might perhaps be thrown on peculiarities in their respective constitutions.

POPULUS BALSAMIFERA.

The first plant experimented on was the *Populus balsamifera*, as representing the numerous family of the poplars. A quantity of the smaller branches of this tree, cut into pieces, was exhausted with boiling water. The dark-brown, bitter liquid was evaporated to the consistence of an extract, and the residue heated for twenty-four hours with dilute nitric acid. A large quantity of nitrous fumes was evolved, and at the same time the odour of an aromatic oil became perceptible. The acid liquid was evaporated to dryness on the water-bath, the residue dissolved in a considerable quantity of hot water, and after cooling, carefully filtered through a cloth. The

* Ann. Ch. Pharm. LXXVIII, 1.
† Ann. Ch. Pharm. LXXIV, 278.

clear liquid was evaporated on the water-bath, and after cooling, exactly saturated with carbonate of potash, an excess of the latter being carefully avoided. A yellow precipitate immediately appeared, and increased after standing for some time. This precipitate consisted of nitropicrate of potash, and the potash-salt of a new acid, to which the author gives the name of *Nitropopulic acid.* The mother-liquid contained a large quantity of nitrate and oxalate of potash. The precipitated mixture of the two first-mentioned salts was collected on a filter, washed with a small quantity of cold water, and pressed to remove the adhering mother-liquid. It was then stirred in a mortar, with dilute carbonate of potash, in which the nitropopulate of potash dissolved without the aid of heat, while the nitropicrate remained undissolved. The two salts were then separated by filtration, and the filtrate containing the nitropopulate slightly supersaturated with hydrochloric acid. The nitropopulate of potash was thereby separated in the form of a compact crystalline powder, which was collected on a filter, and washed with a small quantity of cold water. To remove every trace of adhering nitropicric acid, it was subjected to a second treatment with carbonate of potash, and then repeatedly crystallised from hot water, with the addition of animal charcoal. An excess of alkali must be avoided in these crystallisations, as the nitropopulic acid, when heated, is decomposed by it. The nitropopulate of potash thus purified is of a light lemon-yellow colour. When it is boiled with a large excess of hydrochloric acid, and the solution left to cool, nitropopulic acid separates in slender, needle-shaped, yellow crystals, aggregated in concentric groups; nitric acid cannot be used for this purpose, as it rapidly converts nitropopulic acid into nitropicric acid. Nitropopulic acid, obtained by the process just described, is still contaminated with a yellow substance, which adheres to it with great obstinacy. The crystals must therefore be redissolved in the dilute hydrochloric acid, and afterwards repeatedly crystallised from hot aqueous solutions, with the addition of animal charcoal.

The crystals in their purest state are nearly colourless; the solution is pale-yellow. The pure acid must be quickly freed from the mother-liquid by pressure between bibulous paper, and then dried *in vacuo,* since it would soon turn yellow if exposed to the air in the moist state. When the acid separates slowly from dilute aqueous solutions, it forms hard prismatic crystals, united in concentric groups; but a strong aqueous solution, quickly cooled, yields a magma of delicate silky needles. Hydrochloric acid prevents nitropopulic acid from oxidating; consequently, the latter may be obtained in colourless crystals, from dilute solutions containing hydrochloric acid. Nitropopulic acid is very easily soluble in water, and in a still greater degree in alcohol, both strong and dilute. The addition of sulphuric or hydrochloric acid greatly diminishes its solubility in

water, and at the same time partly destroys the colour of the liquid; on diluting the acid solution with water, the original yellow colour is reproduced. When a solution of nitropopulic acid in dilute hydrochloric acid, is boiled with a larger quantity of the former than it can take up, the undissolved portion fuses into a yellow oil, which solidifies and crystallises on cooling. Nitropopulic acid may likewise be heated with sulphuric acid without suffering decomposition, and crystallises out unaltered as the liquid cools. But by boiling with strong nitric acid, it is converted into nitropicric acid. When boiled with a mixture of hydrochloric acid and chlorate of potash, it is decomposed, and *chloranile* is formed. When the acid is treated with a cold solution of chloride of lime, no action is perceptible, and moreover the liquid may be heated nearly to the boiling-point without decomposition; but on boiling for a few minutes, a sudden effervescence takes place, and chloropicrine is evolved in large quantity. This reaction is characteristic of nitropopulic, indigotic, and chrysammic acid, and furnishes us with the means of distinguishing these acids from nitropicric and oxipicric acids, inasmuch as the latter evolve chloropicrine with solution of chloride of lime, even in the cold, or on the application of a gentle heat. Nitropopulic acid may likewise be distinguished from the acids above-mentioned by the peculiar behaviour of its potash-salt, which is very sparingly soluble in cold water, but dissolves readily in alkaline liquids, and is precipitated therefrom by acids. The potash-salts of nitropicric, oxypicric, and chrysammic acids, on the contrary, are less soluble in excess of alkali than in pure water; whereas indigotate of potash, which, like the nitropopulate, is more soluble in excess of alkali than in water, is nevertheless distinguished from the latter by its greater solubility in cold water, and by being more quickly decomposed by acids.

The taste of nitropopulic acid is very peculiar; it is at first strongly acid, like oxalic acid, then astringent, and afterwards strongly bitter. The solutions of this acid impart a permanent yellow stain to the skin. The dry acid, when moderately heated in a retort, sublimes and crystallises again on cooling. Heated on a platinum spatula, it burns with a bright flame; its salts, when similarly treated, explode with considerable violence. Nitropopulic acid produces a dark-red colour with sesquichloride of iron, and yellow with the protochloride.

The formula of nitropopulic acid, dried *in vacuo*, was found to be:

$$C_{14}H_4N_2O_{14}, \text{ or } C_{14}H_3N_2O_{13}+HO;$$

and that of the acid dried in the air:

$$C_{14}H_4N_2O_{14}+2\text{ Aq.}, \text{ or } C_{14}H_3N_2O_{13}\,.\,HO+2\text{ Aq.}$$

The potash, soda, and silver-salts of this acid, are formed by replacing the atom of basic water by an atom of the respective metallic oxides (or one atom of the hydrogen by the corresponding metal).

With baryta, the acid forms a salt of similar constitution, and likewise a basic salt, containing: $2\,BaO$, $C_{14}H_3N_2O_{13}$.

The *Populus nigra*, treated in a similar manner with nitric acid, likewise yielded nitropopulic acid, together with nitropicric acid. It may therefore be assumed, with some degree of probability, that other species of poplar will likewise yield nitropopulic acid, and that this compound is characteristic of the genus *Populus*.

The *Salix Russelliana*, or Bedford willow, yielded an extract, which, when treated with dilute nitric acid, produced a large quantity of oxalic and nitropicric acid, but no nitropopulic acid.

The following trees and shrubs, treated with nitric acid, likewise yielded oxalic acid and nitropicric acid: *Cytisus laburnum*, *Swietenia mahagoni* (the mahogany-tree), *Pyrus malus*, *Cratægus oxyacantha*, *Ribes nigrum*, *Betula alnus*, *Ulex Europæus*, *Calluna vulgaris*; the roots of *Curcuma longa* (turmeric); the seed-extract of *Bixa orellana* (anotto); *Sambucus nigra*, *Cytisus scoparius* (*Spartium scoparium*, Linn.) — Extracts of *Quercus robur* and *Betula alba*, treated with nitric acid, yielded nothing but oxalic acid, no nitropicric acid or any other acid containing nitrogen being formed. These results appear to show that a far greater number of plants are capable of yielding nitropicric acid than is generally supposed, and that those which form an exception to the rule constitute but a small majority.

SPARTIUM SCOPARIUM.

Some interesting circumstances having been observed during the preparation of the extract of broom, before treating it with nitric acid, the author was induced to submit it to a further examination. When an aqueous decoction of this plant was concentrated to $\frac{1}{10}$th of its bulk, and set aside for twenty-four hours, it solidified into a greenish-brown, gelatinous mass, which was collected on a cloth filter, and washed with cold water. This very impure gelatine consisted chiefly of a crystalline yellow colouring matter (*Scoparine*), contaminated with chlorophyll and oxide of iron, the latter proceeding from the vessel in which the decoction was made. There was also, however, a small quantity of a volatile organic base (*Sparteine*). To purify the scoparine, the crude mass was dissolved in boiling water acidulated with hydrochloric acid; the solution filtered, and left to coagulate by cooling; the mother-liquid removed by pressure; and the mass evaporated to dryness, pulverised, and again dissolved in boiling water: the greater part of the chlorophyll then remained dissolved. The chlorophyll may likewise be separated by continued boiling, or by allowing the solution to cool down to a certain point before filtration. The gelatinous scoparine, purified by either of these methods, and dried in the air or *in vacuo*, at a gentle heat, forms a pale-yellow, or frequently a greenish-yellow, brittle mass,

which is perfectly amorphous. It is very sparingly soluble in cold water, somewhat more soluble in cold alcohol, and dissolves easily in boiling water and alcohol. The aqueous solution is pale-yellow, with a greenish tinge; the alcoholic solution, pale yellow. Scoparine dissolves with peculiar facility in caustic alkalis and alkaline carbonates, forming solutions of an intense yellowish-green colour. When scoparine is dissolved in a small quantity of ammonia or carbonate of soda, and the solution supersaturated with hydrochloric or acetic acid, a white precipitate is obtained, which is soluble in boiling water; and the solution, when very slowly cooled, yields a small quantity of pale-yellow stellate crystals, which collect on the sides of the vessel, while the greater part of the scoparine is deposited in the middle, in the form of a jelly. Scoparine is, however, more easily obtained in the crystalline form by spontaneous evaporation of an alcoholic solution. Crystals are then deposited similar to those which separate from the aqueous solution; they may be purified by pressure between paper, and recrystallisation from hot alcohol. When these crystals are boiled with a quantity of strong alcohol, not sufficient to dissolve them completely, the undissolved portion appears to pass into a peculiar state, and becomes difficultly soluble in water. By solution in ammonia and precipitation by acetic acid, it is converted into a jelly, which is as soluble as the substance in its original state; and on dissolving this gelatinous mass in hot water, and leaving the solution to cool slowly, the characteristic crystals of scoparine are again obtained.

Scoparine prepared by either of the preceding methods has always the same composition. It is tasteless and inodorous, and has no reaction either on litmus or turmeric paper. It dissolves very easily in alkalis and alkaline carbonates, and to a certain degree in strong acids, forming greenish-yellow solutions, which are decomposed by boiling, and yield a greenish-brown resinous substance; it is likewise soluble, though less easily, in baryta and lime-water. A solution of chloride of lime colours scoparine dark-green. Nitric acid converts it into nitropicric acid. By contact with bromine, it acquires a dark-green colour, but does not form a crystalline compound. Solutions of scoparine are not precipitated by nitrate of silver or corrosive sublimate. With neutral and basic acetate of lead it forms greenish-yellow, flocculent precipitates, apparently of variable composition. Scoparine dried *in vacuo* undergoes no further alteration when heated to 100°. When heated in a glass tube, it swells up and becomes charred, but does not sublime. Heated on a platinum spatula, it burns with a light yellow flame.—Scoparine is a powerful diuretic, and is, in fact, the diuretic principle of the *Spartium scoparium*.

The analysis of scoparine agrees with the formula $C_{21}H_{11}O_{10}$.

This formula, however, is only empirical, as no solid compound of the substance has yet been formed from which its composition can be determined.

Sparteine.—The acid mother-liquor of crude scoparine was concentrated by evaporation, and distilled in a capacious retort with a considerable excess of soda. A colourless, heavy oil, then passed over and sank to the bottom of the watery distillate. This oil is sparteine. It is transparent when first prepared, but soon becomes milky by contact with water. When exposed to the air for a few days, it turns brown. It is heavier than water, has a faint odour like that of aniline, and an extremely bitter taste. It has a strong alkaline reaction, and neutralises acids completely. It combines instantly with hydrochloric acid, but does not fume when brought near that acid, being indeed but slightly volatile; it likewise combines with nitric acid, but is decomposed when boiled for a long time with that acid in its concentrated state, yielding products which have not been fully examined. It is also decomposed by boiling with excess of hydrochloric acid, the solution then acquiring an odour like that of mice. Sparteine, in contact with bromine, forms a brown resin, the action being attended with considerable evolution of heat. Sparteine does not yield aniline by distillation with caustic potash, and produces no particular reaction with solution of chloride of lime. The formula of sparteine is $C_{15}\,H_{13}\,N$.

The sulphate, hydrochlorate, and nitrate of sparteine are exceedingly soluble, and very difficult to crystallise. The *nitropicrate* forms long, slender, brittle needles, which cannot be distinguished in appearance from nitropicrate of potash. Its formula is $C_{15}\,H_{13}\,N\,.\,HO\,.\,C_{12}\,H_2\,N_3\,O_{13}$. The *chloride of platinum and sparteine* crystallises in rectangular prisms containing 2 equivalents of water, which go off at 266°. Its formula, when dried at 212°, is $C_{15}\,H_{13}\,N.\,HCl + Pt\,Cl_2 + 2\,HO$. *Chloride of mercury and sparteine* crystallises in large right rhombic prisms, exhibiting the diamond lustre. Its formula is $C_{15}\,H_{13}\,N.\,HCl + HgCl$. A solution of sparteine in hydrochloric acid, mixed with chloride of gold, forms a yellow crystalline precipitate, which is very sparingly soluble in water and alcohol. On adding sparteine to a solution of neutral chloride of copper, a green precipitate is formed containing sparteine, and probably consisting of a double salt. Similar compounds are formed with the neutral and the basic acetate of lead.

Sparteine appears to be a strong narcotic poison, though much inferior in this respect to either nicotine or coneine. It is plain, therefore, that in employing a decoction of broom-tops in dropsical affections, as has hitherto been the practice, the patient is subjected to the narcotic influence of the sparteine, as well as to the diuretic effects of the scoparine, a result which in general is not likely to be

desirable. The author does not, however, think it is at all necessary to use chemically pure scoparine for medical purposes. If a decoction of broom be evaporated to dryness in the water-bath, then treated with a little dilute hydrochloric acid, the mixture thrown on a filter, and washed with a small quantity of cold water, almost all the sparteine will be removed, and the dark-green gelatinous mass remaining on the filter will be found to possess the diuretic, without the narcotic properties of the plant.

Process for Determining the Amount of Hydrocyanic Acid in Medicinal Prussic Acid, Bitter Almond Water, and Laurel Water.
By Justus Liebig.

When a liquid containing hydrocyanic acid is mixed with caustic potash till it exhibits a strong alkaline reaction, and a dilute solution of nitrate of silver slowly added to it, a precipitate is formed, which, up to a certain limit, immediately disappears again on ignition. If the hydrocyanic acid be mixed with caustic potash and a few drops of solution of common salt, it will be found that the first portions of silver-solution added to the mixture do not produce a permanent precipitate; the precipitate, when it does appear, is white in this latter case, and consists of chloride of silver.

The hydrocyanic acid liquid mixed with caustic potash contains cyanide of potassium, in which oxide or chloride of silver is soluble, up to the point at which the known double-salt composed of single equivalents of cyanide of potassium and cyanide of silver is formed, that compound not being decomposed by excess of alkali.

If then we know the quantity of silver contained in a solution of the nitrate, and likewise the quantity by weight or volume which must be added to a liquid containing alkali and hydrocyanic acid, to produce a permanent precipitate, the proportion of cyanogen or hydrocyanic acid contained in the liquid will thereby be determined; for one equivalent of silver corresponds exactly to two equivalents of hydrocyanic acid. This method is, in fact, found to give results agreeing as nearly as possible with those obtained by the direct method of precipitating the cyanogen as cyanide of silver, and weighing the precipitate. In a sample of dilute hydrocyanic acid, in which the direct method showed the presence of 0·067 per cent of hydrocyanic acid, the proportion determined by mixing the liquid with potash, and then adding a measured quantity of silver-solution of known strength, till the liquid after strong agitation remained slightly milky, was in one experiment 0·068, and in another 0·067. In another sample containing 0·0466 per cent of hydrocyanic acid, as

determined by the direct method, the proportion found by mixing the liquid with potash and a small quantity of common salt, and then adding the measured silver-solution, was 0·0476 per cent. By adding the same silver-solution from a graduated measure till the whole of the hydrocyanic acid was precipitated, the proportion found was 0·0469 per cent.

These experiments show that the determination of the amount of hydrocyanic in an alkaline liquid by means of a graduated silver-solution, is not inferior in point of accuracy to the best methods generally adopted, while it far exceeds them in expedition and facility of execution. The presence of formic or hydrochloric acid, which would render the estimation of hydrocyanic acid by the ordinary method of precipitation, by means of a graduated silver-solution, inexact, has no influence whatever on its determination in an alkaline liquid. The latter method has likewise the great advantage of showing at once, by the appearance of a permanent milkiness, when the operation is at an end; whereas, in adding the graduated silver-solution to an acid liquid containing hydrocyanic acid, it is necessary to wait for the precipitate to settle down, before the operator can know whether any more is to be added; and from a dilute solution, the last traces of cyanide of silver take a long time to separate.

For druggists, who do not possess accurate measures, and are, therefore, obliged to make their experiments by weighing, the following proportions may be useful.

63 grains of fused nitrate of silver are to be dissolved in 5937 grains of water, so as to form 6000 grains of a liquid, 300 grains of which correspond to 1 grain of anhydrous hydrocyanic acid.

To test a sample of aqueous hydrocyanic acid, the vessel containing the silver-solution just mentioned is to be weighed, and the solution then added to a weighed portion of the hydrocyanic acid previously mixed with potash-ley and a few drops of solution of common salt (*e. g.* 60 grains of the aqueous acid diluted with three or four times its bulk of water); the hydrocyanic acid may be contained in a common white medicine-glass, and the addition of the silver-solution must be continued till a visible turbidity is produced, and does not disappear on agitation. The silver-solution is then weighed again, and the quantity used determined by the loss. Supposing that 360 grains of silver-solution have been used; then the 60 grains of aqueous acid contain 1·20 grains of anhydrous hydrocyanic acid, or the sample contains 2 per cent. In testing by this method, an error of a grain or two in the quantity of silver-solution used is not likely to occur; but even this would only make a difference of $\frac{1}{100}$ or $\frac{1}{50}$ of a grain in the amount of hydrocyanic acid.

The same method may be used for estimating the proportion of hydrocyanic acid in bitter almond water and laurel water. The latter is generally clear and transparent; but the former is often rendered

milky by the presence of little drops of oil, and it is therefore necessary to dilute it with three or four times its bulk of water to render it clear; otherwise the limit of the reaction cannot be exactly seen. A number of experiments made with laurel water showed that it contained 1 part in 10,000 of anhydrous hydrocyanic acid, and bitter almond water was found to contain $7\frac{1}{2}$ parts in 10,000.

The method may likewise be used for the valuation of commercial cyanide of potassium, and its application in this way has led to the unexpected result, that that substance, as prepared by Liebig's method, is much less rich in cyanide of potassium than was formerly supposed. In two samples prepared by different operations, the proportions found were 63·5 and 59·99 per cent.

New Method of Determining the Proportion of Oxygen in Atmospheric Air.

By Justus Liebig.

The researches of Chevreul and Döbereiner have shown that an alkaline solution of gallic or pyrogallic acid will absorb the whole of the oxygen from the air, the former slowly, the latter with great rapidity. This property is now proposed by Liebig as the foundation of a method of eudiometry, not with the view of superseding the complete methods of Regnault, Bunsen, Dumas and Boussingault, and others, but as a means of quickly arriving at a very near approximation, in researches requiring a great number of analyses of air, and in which it is desirable that these analyses shall be made with expedition, and without the use of complicated apparatus,—as for instance, in investigations connected with the physiology of respiration, or the examination of the air which issues from furnaces, &c.

The following is the mode of proceeding, to determine both the carbonic acid and the oxygen in the air. The air is contained in graduated tubes standing over mercury, and occupies about $\frac{2}{3}$ of the length of the tubes. Potash-ley, of specific gravity 1·4 (1 part of dry hydrate of potash to 2 parts of water) is then introduced in quantity equal to $\frac{1}{30}$ or $\frac{1}{40}$ of the volume of the air, by means of a curved pipette; the tube moved quickly up and down to spread the liquid over the inner surface; and the volume of the air read off as soon as it has become constant. If the air has been previously dried by chloride of calcium, the quantity which disappears gives exactly the amount of carbonic acid; but if the air is moist, the determination is affected with an error arising from the absorption of aqueous vapour by the strong caustic potash.

The carbonic acid being thus determined, a solution of pyrogallic

acid, containing 1 grm. of the acid in 5 or 6 cubic centimeters of water, and equal in volume to half that of the caustic potash, is introduced into the same tube by means of another pipette, and the tube agitated as before. The absorption of the oxygen is complete in about two minutes, and the residual gas may then be read off.

A slight error arises from the diminution of the vapour-tension of the potash-ley, consequent on diluting it with the solution of pyrogallic acid. It is, however, scarcely appreciable, and may be altogether prevented by passing up into the liquid a piece of hydrate of potash, just sufficient to saturate the water contained in the pyrogallic acid, and waiting till it is dissolved before reading off the volume. The results obtained by this method accord very nearly with the best analyses of air.

Ordinary gallic acid may likewise be used instead of pyrogallic acid; as, however, it is very sparingly soluble in water, it must be used in the form of a solution of gallate of potash. When this solution is added to the caustic-potash in the graduated tube, the liquid absorbs the oxygen of the air in the tube, and assumes a dark-red colour; when this colour is no longer produced, the operation is ended. The results obtained by this method are not so accurate as those obtained by the use of pyrogallic acid, because the absorption goes on slowly, taking an hour and a half or two hours, instead of a few minutes, and errors consequently arise from change of pressure and temperature in the air during the progress of the experiment. Tannic acid may also be used as an absorbing agent, but its action is even slower than that of gallic acid.

The only objection to the use of pyrogallic acid is its comparative costliness. It may, however, be advantageously obtained by subjecting the so-called Chinese gall-nuts to destructive distillation in small retorts, capable of containing 5 or 6 ounces of the nuts in crude lumps. A very concentrated solution of pyrogallic acid then passes over; and this, when evaporated over the water-bath, yields crystallised pyrogallic acid, amounting to 15 per cent of the gall-nuts used. Another mode of obtaining this acid is by sublimation from the watery extract of the gall-nuts, just as benzoic acid is obtained from gum-benzoin: the product amounts to 10 per cent of the extract.

The methods of eudiometry above described are affected with an error which can scarcely be obviated. This error arises from the adhesion of the liquid to the sides of the graduated tubes, and the consequent difficulty of reading off its volume with accuracy. By always operating on the same original volume of air, this error may be diminished, so far, at least, as to be of little consequence in comparative analyses; but for absolute determinations, the more exact methods of **Dumas and Boussingault, Regnault and Reiset, or Bunsen**, are indispensable.

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XX.—*On the Equivalent of Phosphorus.*

By A. Schrötter.

FROM A LETTER TO A. W. HOFMANN.

I have already informed you of my being at present engaged in determining the equivalent of phosphorus and of some other elements of the same group; and I have also given you a general idea of the method by which I hoped to obtain accurate results. I am now enabled to lay before the Chemical Society the results I have obtained with regard to phosphorus.

Ten combustions of amorphous phosphorus, in perfectly dry oxygen, gave for one part of phosphorus, the quantities of phosphoric acid stated in the second column of the following table. The third column contains the equivalent of phosphorus calculated from each determination:

1.	2·28909	31·0290
2.	2·28783	31·0600
3.	2·29300	30·9358
4.	2·28831	31·0484
5.	2·29040	30·9981
6.	2·28788	31·0588
7.	2·28848	31·0443
8.	2·28856	31·0424
9.	2·28959	31·0183
10.	2·28872	31·0386

The mean of these experiments gives for one part of phosphorus, 2·289186 of phosphoric acid, corresponding to the equivalent 31·0274.

The amorphous phosphorus employed for these experiments was perfectly pure, and was used in fragments, and not as a powder; the fragments having been exposed for some time to a temperature of 150°, in some cases in carbonic acid gas, in othes in hydrogen. The combustion-tube being fixed between two series of drying-tubes, one of which stood in connection with two gas-holders, the other with the atmosphere, the combustion could be so regulated that not the slightest loss was incurred. A tube filled with anhydrous phosphoric acid inserted in place of the combustion-tube, showed not the slightest increase in weight after a current of air had been drawn through the apparatus for some time. The entire removal of the oxygen remaining after the combustion was effected by passing a current of atmospheric air from the second gas-holder. A correction for the weight of the air in the tube was not necessary, since all the numbers in the table are differential numbers, and consequently only a slight error would be introduced into the results by the variation of temperature and pressure during the progress of the experiments. In order to remove every trace of a lower oxide, the phosphoric acid was sublimed in an atmosphere of oxygen.

The close approximation existing between the numbers obtained, is the clearest proof that all causes of error were reduced to a minimum. If it be also remembered that an error of 1 milligramme in the denominator of the fraction by which the equivalent is obtained, gives rise to a corresponding error of 0·0187 in the equivalent, the true equivalent of phosphorus may be taken at 31. In fact, all the sources of error in the experiments tend to diminish the quantity of oxygen consumed (which quantity is made the denominator of the fraction above alluded to), and therefore to render the equivalent somewhat too high. The mere circumstance, that in all the experiments a little phosphorus may have fused into the glass etched by the phosphoric acid, and thus have escaped combustion, suffices to explain the small excess obtained.

From this it is evident that the number 31·60, given by Berzelius, approaches nearer to the true equivalent of phosphorus than that found at a later period by Pelouze, namely, 32.

Further details you will find in the paper which will appear in the second part of the third volume of the "Denkschriften der K. Academie."

XXI.—*On Dibenzoylimide, a new derivative of Oil of Bitter Almonds.*

By Joshua H. Robson.

Among the host of compounds which have been obtained from oil of bitter almonds, few have a higher claim to the attention of chemists, than the hydrobenzamide of Laurent, especially since we have become acquainted with the remarkable molecular change, first pointed out by Fownes, of this substance under the influence of potassa, when, as is well known, the neutral hydrobenzamide is converted, without change of composition, into the basic amarine (benzoline). A closer examination of amarine, a base of such definite origin, promised to throw much light upon the constitution of the bases containing 2 equivalents of nitrogen, such as furfurine, fucusine, &c.

It was with this object in view that I began to work on oil of bitter almonds. This substance, however, is of so peculiar a composition, the elements therein appear to be arranged in a manner liable to so many changes, that it appears scarcely possible to touch it without producing some new substance. And so it happened, that when endeavouring to prepare the hydrobenzamide, intended to be converted into amarine, I became acquainted with a new reaction, which I had to study before prosecuting the original direction of the inquiry.

On passing a current of ammonia into a solution of oil of bitter almonds in alcohol, a large quantity of the gas is absorbed. This solution, on standing for some hours, deposits a more or less granular compound, together with a resinous substance. The granular substance is entirely insoluble in alcohol, by which means it may be purified. It then consists of a white powder, to which I shall return presently. The substance deposited from the alcohol, (which was believed to contain a great deal of hydrobenzamide), was boiled with a strong solution of potassa for some hours, in order to convert the substance into amarine, when it assumed a bright red colour, and became quite brittle and resinous. It was then heated with a highly dilute solution of hydrochloric acid, for the purpose of dissolving out the amarine. The salts of this base being remarkably insoluble, it was found necessary to boil it with successive portions of dilute acid, until addition of ammonia to the solution failed to produce a precipitate. Notwithstanding this, the quantity of amarine obtained in my repeated experiments was very small, clearly showing that the substance deposited from the alcohol contained but a trifling quantity of hydrobenzamide. The resinous mass remaining was then heated with

boiling alcohol, which dissolved a considerable portion, leaving a yellowish powder,—almost entirely insoluble in ether, but more soluble in boiling wood-spirit, being deposited therefrom on cooling,—in brilliant feathery crystals. This substance, the principal product of the reaction, was found by analysis to have the following composition :

I.	0·1769	grm.	of substance gave
	0·5177	„	„ carbonic acid, and
	0·1060	„	„ water.
II.	0·1416	„	„ substance gave :
	0·407	„	„ carbonic acid, and
	0·0805	„	„ water.
III.	0·1811	„	„ substance gave :
	0·5272	„	„ carbonic acid, and
	0·1032	„	„ water.
IV.	0·6054	„	„ substance, burnt according to Dumas' method, gave:
	52·5	c.c.	of nitrogen, at 15° C. and 757^{mm}. 5 Bar.
V.	0·1755	grm.	of substance gave:
	0·1764	„	„ ammonio-chloride of platinum.
VI.	0·1259	„	„ substance gave :
	0·1250	„	„ ammonio-chloride of platinum.

To these numbers correspond the following percentages :

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	79·81	79·03	79·84	—	—	—
Hydrogen . .	6·67	6·3	6·33	—	—	—
Nitrogen . .	—	—	—	6·807	6·33	6·3

The simplest expression agreeing with these results, is the formula

$$C_{28}\,H_{13}\,NO_2,$$

which requires the following values :

		Theory.		Experiment.
28 equivs. of	Carbon. . .	168	79·62	79·56
13 „ „	Hydrogen . .	13	6·16	6·43
1 „ „	Nitrogen . .	14	6·60	6·49
2 „ „	Oxygen . .	16	7·62	
		211	100·00	

The formation of this new compound, (for which, as long as a definite nomenclature for the substances produced by ammonia is not established, I propose the provisional term *Dibenzoylimide*) is very simple. It is due to the action of 1 equivalent of ammonia upon 2 equivalents of oil of bitter almonds, 2 equivalents of water being eliminated:

$$2\,(C_{14}\,H_6O_2)+N\,H_3=C_{28}\,H_{13}\,NO_2+2\,HO.$$

The formation of dibenzoylimide, is perfectly analagous to that of imesatine, one of the products of the action of ammonia upon isatine.

$$2\,\underbrace{(C_{16}\,H_5\,NO_4)}_{\text{Isatine.}}+N\,H_3=\underbrace{C_{32}\,H_{11}\,N_3\,O_6}_{\text{Imesatine.}}+2\,HO$$

It is evident that the hydrocyanic acid, which is present in oil of bitter almonds, has nothing to do with the formation of this compound, which was confirmed, moreover, by the fact, that perfectly pure hydride of benzoyl exhibited exactly the same deportment.

Dibenzoylimide dissolves in hot nitric acid, from which it crystallises on cooling; but on boiling it for some hours, it no longer does so; on diluting with water, a substance of bright yellow colour is precipitated. This substance dissolves in concentrated sulphuric acid, but without colouring it, and on the addition of water it is again thrown down. An alcoholic solution of ammonia dissolves it with a bright red colour. An alcoholic solution of potassa produces the same effect. It dissolves in boiling alcohol, from which it separates on cooling, but not in a crystalline form. The substance has doubtless assimilated the elements of hyponitric acid.

Sulphuric acid dissolves dibenzoylimide with a bright red colour, from which it separates on dilution with water.

Hydrochloric acid, after being boiled with the substance for some hours, does not change it.

Aqueous solution of potassa, on being boiled with the substance for some time, does not affect it.

Alcoholic solution of potassa, on boiling with it for some days, gradually reconverts it into oil of bitter almonds, ammonia being disengaged.

Before concluding the description of dibenzoylimide, I must briefly mention some peculiar changes which this substance appears to suffer under the influence of soda-lime. In determining the nitrogen, I experienced some difficulty, inasmuch as part of the substance appeared to sublime through the soda-lime employed, without being altered; I accordingly made the analysis No. III. by Dumas' method; but as this process gave but slightly differing results, I

returned again to the soda-lime process. In all these analyses, a beautiful yellow crystalline substance sublimed at the mouth of the combustion-tube, which on fusing with potassium, and testing with the salts of iron, was however found to contain no nitrogen. This substance dissolved in concentrated sulphuric acid with a beautiful violet colour, which showed at once that it differed from the original compound. To produce this substance, about a gramme of the dibenzoylimide was mixed with soda-lime and distilled; a small quantity of it was again produced, but now, together with a yellow powder, which collected in a cooler part of the tube, and which was found to contain nitrogen: the latter dissolved in concentrated sulphuric acid, producing a splendid crimson colour. It is very probable that this was a mixture of the non-nitrogenized body with the undecomposed original substance. All my attempts to obtain a sufficient quantity of the non-nitrogenised compound in a state of purity failed; I found it to be entirely insoluble in alcohol, wood-spirit, or ether.

In the commencement of this paper, a granular substance was mentioned, which was left behind on purifying the crude product of the action of ammonia upon oil of bitter almonds with alcohol. It remains only to state that this substance, both by the study of its physical properties, and by analysis, was found to be identical with a substance lately obtained by Messrs. Laurent and Gerhardt in the treatment of oil of bitter almonds with ammonia.

I. 0·1135 grm. of substance gave:
0·338 „ „ carbonic acid, and
0·0568 „ „ water.
II. 0·2339 „ „ substance gave:
24·00 c.c. of nitrogen, at 12° C. and 760^{mm}. Bar.

These numbers lead to the following percentage, which I contrast with the theoretical value of the formula

$$C_{30} H_{12} N_2.$$

	Theory.		Experiment.
30 equivs. of Carbon .	180	81·8	81·21
12 „ „ Hydrogen .	12	5·4	5·55
2 „ „ Nitrogen .	28	12·8	12·20
	220	100·0	98·96

This substance forms by the coalescence of 2 equivalents of oil of bitter almonds and 1 equivalent of cyanide of ammonium, from which 4 equivalents of water are separated:

$$2 C_{14} H_6 O_2 + NH_4 Cy = C_{30} H_{12} N_2 + 4 HO.$$

By boiling it for a considerable time with hydrochloric acid, it is split, in accordance with its formation, into hydrocyanic acid and oil of bitter almonds, which distils over, ammonia remaining with the hydrochloric acid. According to Messrs. Laurent and Gerhardt, it is very probable that this substance is identical with the benzhydramide, but imperfectly investigated by the latter chemists, and which still figures in all the chemical manuals.

In conclusion, I beg to tender my sincere thanks to Professor Hofmann, for the valuable assistance which he has afforded me during this investigation.

XXII.—*On Etherification.*

By Alexander W. Williamson, Ph.D., F.C.S.

Professor of Practical Chemistry in University College, London.

The question of the transformation of alcohol into ether and water by the agency of sulphuric acid, may be divided into two parts; first, the relative weight of the substances engaged in the reaction; and, secondly, the actual process by which the transformation is effected. In a preceding memoir, read before the British Association last autumn, I briefly described the formation and properties of certain new ethers, which seemed to solve at least the first part of this question, *i. e.* the relative formulæ of alcohol and ether. I now lay before the Society a more exact account of the process by which these bodies were obtained, with their analysis, to which I have to add a direct evidence of the process by which sulphuric acid effects the decomposition of alcohol; and, finally, I will describe a reaction with the acids of the adipic series, in which the formation of a peculiar series of bodies gives evidence that the formulæ of these acids should be halved similarly to those of the alcohols. But first, a few words on the previous views of the subject, as I understand them.

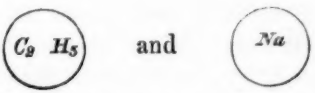
Of the relative formulæ of alcohol and ether, there have been especially two views; one of which represented ether as the compound of olefiant gas with one atom of water, and alcohol as the compound of this same hydrocarbon with twice as much water; the other considered ether as the oxide of a peculiar hydrocarbon C_4H_{10}, and alcohol as the oxide of another hydrocarbon C_2H_6. The first of these views was derived from a consideration of the analogy of the ethers with the salts of ammonia; the second was formed rather from a comparison with metallic salts. To the French school, with Dumas

at its head, we owe the former, and the great Berzelius suggested and advocated the latter. The study of the transformations of alcohol, and especially that by sulphuric acid, led to the modification of these views, and to the formation of others containing certain points of each; and the most important of these is certainly the theory of Liebig, who, giving the name of ethyl to the hydrocarbon $C_4 H_{10}$, represented ether as its oxide, and alcohol as the hydrate of that oxide. From novel and highly important considerations, Gerhardt arrived at the formulæ of Berzelius, and compared alcohol in its reactions to an acid. The process of etherification, of which the continuous nature had been discovered by Boullay, was, from the different points of view afforded by the above-mentioned formulæ, of course represented differently. Berzelius and the contact-school, seeing in ether a more complex atom than alcohol, and considering the apparently indefinite action of sulphuric acid, were especially struck with the difference between etherification and other cases of chemical action, and supposed some different force must be active in it, which was christened *catalysis*. It was certainly an important step towards the philosophical solution of the question, which Liebig made, in urging the resemblance to chemical action, and explaining more successfully than Hennel had been able to do, the process by chemical affinity, overcome successively by the decomposition of sulphovinic acid by heat. The mutual action of these various theories had exercised a decomposing influence upon them all, and the elegant experiments by which Graham shewed the untenable nature of the chemical theory, afford conclusive evidence of that decomposition. Now I submit that the theory here laid before you, with its experimental conclusions, combines the requisitions of the several parties in this great discussion, and may be considered as closing it amicably, by shewing that each point of view contained part, and an important part, of the facts. The explanation of the process is composed of two parts—first, proving in etherification the occurrence of decompositions strictly analogous to common phenomena usually attributed to chemical affinity, and as explicable by such a name as those phenomena may be; and, secondly, on finding that over and above the commonly observed phenomena of chemical action, there occurs in this process a new circumstance, it will be necessary to prove the occurrence of this circumstance in the more familiar cases.

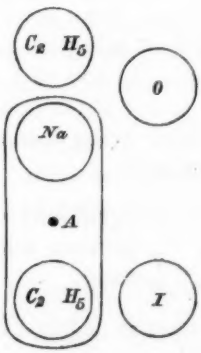
Formation of ether by double decomposition.—In the paper above referred to, I stated the fact of this reaction, which consists in the elimination by metallic sodium of the hydrogen in alcohol, which has to be replaced by ethyle, and the action of the iodide of ethyle

on the compound thus formed, which, from its analogy with the hydrate of potash, I will call *ethylate of potash.** It is important that the alcohol used in this and all similar reactions be as anhydrous as possible; and the naphtha which surrounds the sodium must be removed completely by drying with bibulous paper and immersion for a few seconds in a small portion of absolute alcohol, which serves successively to rinse all the pieces of metal used in one experiment. The pieces of sodium thus purified are thrown, one at a time, into the alcohol which is to be transformed into ether, until the liquid is completely saturated with them; after cooling, it is treated with iodide of ethyle, and distilled, the ether passing over with alcohol vapour and some of the iodide. To remove these admixtures, the distillate should be treated with sodium, which, as long as alcohol is present in equivalent quantity with the iodide, forms more ether, and when all the iodide has been thus decomposed, forms with the remaining alcohol, ethylate of sodium, from which the ether may be distilled off in a state of perfect purity. Prepared in this manner, ether is identical in its boiling-point and all its properties with that prepared by the action of sulphuric acid.

The reaction is easily understood by the following diagram, in which the atoms



are supposed to be capable of changing places by turning round upon the central point A.



* The atomic weight of hydrogen and the metals, iodine, &c., is in this paper according to Laurent and Gerhardt's notation, assumed at half their equivalents. The compound radicals methyle (CH_3), ethyle (C_2H_5), amyle (C_5H_{11}) are of course reduced to the same unit.

It is clear that we thus get $\begin{matrix} C_2 H_5 \\ C_2 H_5 \end{matrix}$ O and NaI. The circles are merely used to separate off the atoms or units of comparison. To express the corresponding decomposition of iodide of ethyle by hydrate of potash, forming alcohol, we should replace the ethyle of the sodium-compound by hydrogen, and the same change of place between sodium and ethyle forms $\begin{matrix} H \\ C_2 H_5 \end{matrix}$ O (alcohol) and Na I.

Three-carbon ether, Ethylate of methyle, or Methylate of ethyle.—This compound may be prepared by the action of iodide of ethyle on the methylate of sodium, $\begin{matrix} CH_3 \\ Na \end{matrix}$ O, or inversely, by acting on ethylate of sodium by iodide of methyle. Of these two processes, I however prefer the former, from the fact of iodide of ethyle boiling at so much higher a temperature than the ether, that any excess of it is easily separated by distillation. This ether is purified in the same manner as the preceding one. On account of its more powerful action, I generally preferred potasssium to sodium for the removal of the last traces of alcohol from an ether; and in order that the action of the metal might be complete, the distilling apparatus was so arranged that the distillate constantly flowed down into the retort until the action had completely ceased, and then only was the ether distilled over from the fixed products of that action. The boiling-point of this ether is 11° C., and it was therefore usually distilled simply by removing from the retort the frigorific mixture by which it was retained in the liquid state. In order to effect its combustion, a small quantity was introduced into a strong bulb at the extremity of a piece of thermometer tubing, about 6 inches long, which had been previously weighed, and which being bent at a right angle, could be fixed by means of a cork into the end of a combustion-tube, open at both ends, and was in the power of the operator.

By this process, the ether being burnt by oxide of copper, the following results were obtained:

0·2215 grm. of liquid gave:
0·482 „ „ carbonic acid, and
0·2685 „ „ water.

The percentage composition as deduced from this, is:

	By Experiment.	By Calculation.	Difference.
Carbon	59·39	60·00	0·61 −
Hydrogen . . .	13·46	13·33	0·13 +
Oxygen	27·15	26·67	0·48 +

The density of its vapour was found to be:

By Experiment.	By Calculation.	Difference.
2·158	2·084	·074

Weight of globe and air at 12° C. and 30·05 in. bar. = 53·6240 grms.
Weight of globe and vapour, the temp. at moment of sealing the point 23°·5 C., and bar. 30·05. . = 54·1790 „
Capacity of globe . . . . . = 438 cub. centi.
Residual air at 16° C. and 30·05 bar. . . = 23 „

Hence its formula is $\begin{matrix} C_2 H_5 \\ C H_3 \end{matrix} O$, or empirically $C_3 H_8 O$.

Now it being thus established beyond doubt that this substance contains 1 volume ethyle, 1 vol. methyle, with 1 vol. oxygen, the three condensed into two volumes, and the two opposite modes of preparing it proving that the two atoms of hydrocarbon are contained in *like* manner in it, we may view it either as the ethylate of methyle, *i. e.* alcohol in which one atom of hydrogen is replaced by methyle, or else as methylate of ethyle. I am, however, convinced that the simplest view that can be formed of its constitution is to be gathered from a comparison with water, from which it may be produced by replacing one atom of hydrogen by ethyle and the other by methyle.

Seven-carbon ether, Amylate of ethyle, or Ethylate of amyle.—This ether is one of the most easily prepared of these peculiar bodies, and is perfectly identical when prepared from amylic alcohol and iodide of ethyle, or ethylic alcohol and iodide of amyle. I have prepared it in considerable quantity by each process, and could discover in no respect any difference of properties between the products; its boiling-point is 112° C. Combustion performed with oxide of copper.

0·2350 grm. yielded:
0·624 „ of carbonic acid, and
0·276 „ of water;

or in 100 parts.

	Experiment.	Calculation.	Difference.
Carbon	72·42	72·41	0·01+
Hydrogen . . .	13·99	13·79	0·20+
Oxygen . . .	13·59	13·80	0·21−

Its formula is therefore $\begin{matrix} C_2 H_5 \\ C_5 H_{11} \end{matrix} O$, or empirically $C_7 H_{16} O$.

The density of its vapour was found to be:

By Experiment.	Calculation.	Difference.
4·042	4·031	0·011

Weight of globe and air at 11° C., bar. at 29·60 in. = 93·7790 grms.
Weight of globe and vapour, the temp. at moment of sealing being 135·5° C., and bar. 29·64. .= 94·6755 „
Capacity of globe . . . . . .= 377 cub. centi.
Residual air at 25° C., and 29·60 bar. . . .= 3 „
Increased expansion of glass globe at 135° C. .= 0·92 „

Six-carbon ether.—Boils at 92° C.; analysis as follows:

0·2050 grm. of liquid gave as the produce of combustion:
0.528 „ „ carbonic acid, and
0·256 „ „ water.

which gives in 100 parts:

	Experiment.	Calculation.	Difference.
Carbon . .	70·244	70·588	0·344−
Hydrogen . .	13·873	13·725	0·148+
Oxygen . .	15·883	15·686	0·197+

Hence the formula $C_6 H_{14} O$.

The density of its vapour was found to be:

By Calculation.	By Experiment.
3·546	3·75

Weight of globe and air, temp. 10° C., bar. 29·72 in. = 90·689 grms.
Weight of globe and vapour, temp. at moment of sealing the point 110° C., and bar. 29·72 in. .= 91·553 „
Capacity of globe . . . . . .= 407 cub. cen.
Residual air at 19½° C., and 29·93 inches bar. .= 10·75 „

A second experiment gave nearly analogous results:

Weight of globe and air, temp. 11·5° C., bar. 30 in. = 85·0855 grms.
Weight of globe and vapour, temp. at moment of sealing, 111·5° C., bar. 30 in. . . . .= 85·8925 „
Capacity of globe . . . . . .= 377 cub. centi.
Residual air at 22° C., and 30 in. bar. . . .= 4·5 „

Calculated density from this latter experiment = 3·73.

In my former paper, I showed how the formation of these intermediate ethers proves the atomic weight of the alcohols to be half

that which they have of late years been considered, so that their equivalent occupies in the state of vapour the same volume as that of ether, water, &c. It is of course only a *relation* which I here establish, and if any chemists prefer doubling the present formulæ of ether, water, and all the metallic oxides, they will accomplish the same object in an unnecessarily clumsy manner. But the same arguments which require me to halve the atomic weight of alcohol must of course apply to its compounds, and sulphovinic acid, which is nothing else than the sulphate of alcohol, as represented by the formula $\frac{Æ}{H} SO_4$; and the process of etherification is at once explained; for by the reaction of this sulphovinic acid upon alcohol, we have at once ether and sulphuric acid, which again reacts upon the atoms of alcohol, forming with the first, $\frac{Æ}{H} SO_4$ and $\frac{H}{H}O$, and with the second $\frac{Æ}{Æ}O$ and $\frac{H}{H}SO_4$. Thus it is that the sulphovinic acid formed at the end of a long process of etherification is not the same as that which formed at first, but being perfectly like, it cannot of course be distinguished from it. To prove this point, I made sulphuric acid react successively upon two alcohols, so that it took the hydrocarbon from the first, and gave it up to the second, forming an intermediate ether, and finding only the second alcohol to react upon, remained at last combined with its hydrocarbon alone. The experiment was performed in the following manner: Sulphamylic acid was prepared by the action of sulphuric acid upon its equivalent weight of fusel oil, and this compound was treated with vinic alcohol by the continuous process, until the distillate consisted of pure 4-carbon ether. The residue was then examined, and found to contain *no* sulphamylic acid, but only sulphovinic, the 7-carbon ether being easily separated out from the first portions of the volatile product. I next tried the action of sulphuric acid upon a mixture of equivalent weights of the two alcohols, expecting similarly to have the production of the 7-carbon ether, and the result fully justified my expectations; for on treating the mixture by the continuous process, a distillate was obtained consisting of two liquids, water and a light ethereal liquid, which, after two distillations over fused potash, was distilled with the thermometer, and rose from 40° to 180°. A considerable portion was separated by repeated distillation at the temperature of 112° C. I shewed by combustion the exact composition of the 7-carbon ether.

0·25075 grm. of ether yielded:
0·6665 „ „ carbonic acid, and
0·3100 „ „ water.

which gives the following percentage:

	Experiment.	Calculation.	Difference.
Carbon	72·46	72·41	0·05+
Hydrogen . . .	13·73	13·79	0·06−
Oxygen . . .	13·81	13·80	0·01+

The last portions of the distillates were added together and redistilled, their temperature rising rapidly to 176°, where it remained stationary for some time, and the liquid which came over at this temperature shewed the composition of amylic ether. Thus:

0·2045 grm of distillate produced:
0·5685 „ „ carbonic acid, and
0·2595 „ „ water.

giving the following percentage composition:

	Experiment.	Calculation.	Difference.
Carbon	75·81	75·95	0·14−
Hydrogen . . .	14·09	13·92	0·17+
Oxygen . . .	10·10	10·13	0·03−

The smell of common ether was very perceptible in the first portions of the mixture which came over. It is thus clear that by the action of sulphuric acid on the mixed alcohols, three ethers are formed by the reaction of sulphovinic and sulphamylic acids on each of the alcohols respectively. On treating in a similar manner a mixture of equivalent parts of methylic and amylic alcohols, a corresponding result was obtained, the products being, however, more easily separated than in the preceding instance, owing to the greater difference of their boiling-points. The experiment was performed in the following manner: 17 oz. of aqueous methylic alcohol was mixed with 38 oz. of fusel oil, which had been ascertained by a previous trial to contain the equivalent quantity of amylic alcohol; 7 oz. of this mixture were added to 5 oz. of sulphuric acid, and heated to 120°, at which temperature the etherification commenced; the mixed alcohols were allowed to run into the retort, so as to maintain the level of the liquid in it a little higher than it had been at first, and in this manner the whole of the mixture was converted into a colourless distillate, composed of about one volume of

water to three of the mixed ethers, and possessing a faint smell of sulphurous acid. The theory of the purification of this mixture by distillation over dry hydrate of potash, is easily intelligible from the fact that that substance becomes transformed in contact with alcohol into ethylate of potash, with formation of water; and similarly into amylate of potash by the action of amylic alcohol. Thus it is that the whole of these alcohols are kept back by the potash, and the excess of it even takes up pretty completely the water, so that the mixture of ethers, after this treatment, is scarcely acted on at all by potassium. We have in these reactions the best evidence of the nature of the action of sulphuric acid in forming common ether, or in accelerating the formation of the so-called compound ethers; for acetic ether is formed from acetic acid, just as ethylic ether from alcohol, by the replacement of hydrogen by ethyle. And if the circumstance of containing hydrogen, which is replaceable by other metals or radicals, be the definition of an acid, we must consider alcohol as acting the part of an acid in these reactions. Common ether is its ethyle-salt, the 3-carbon ether is its methyle-salt, and so on, just as the potassium-alcohol or ethylate of potash is its potassium-salt.

But before proceeding further in the investigation of these circumstances, I must beg leave to direct your attention for a moment to the relation between alcohol and acetic acid, and show how the conclusions just arrived at concerning the former will be applicable to the atomic weight of the latter. You are aware that this acid is essentially monobasic in its characters like the other terms of the series to which it belongs, and that, in conjunction with other reasons, this circumstance has been urged by M. Gerhardt as a ground for halving its formula. Now as acetic acid is formed from alcohol by replacing one-third of its hydrogen by oxygen, there are strong grounds for assuming a similar atomic constitution in both, and of writing acetic acid at half its usual atomic weight, in accordance with the reduced formula of alcohol. Viewing, therefore, alcohol as water in which half the hydrogen is replaced by ethyle, $\overset{C_2 H_5}{H} O$, we shall consider acetic acid as containing one equivalent of oxygen in the place of two atoms of hydrogen of that radical, or $\overset{C_2 H_3 O}{H} O$. Organic chemistry is replete with instances of differences similar to those between alcohol and acetic acid, and produced by the substitution of an electro-negative element for hydrogen; take for example phenylic alcohol, a feeble acid, in which the substitution of hyponitric acid for hydrogen

produces stronger and stronger acids up to carbazotic, a very strong acid; or again, consider the diminution of the alkaline properties of aniline by the substitution of more and more chlorine for its hydrogen, until they entirely disappear in the trichloraniline, as shewn by Dr. Hofmann. Now we actually prepare acetic acid by the action of oxygen upon alcohol under certain circumstances, and observe a double decomposition perfectly analogous to that produced by chlorine in its action on hydrocarbons, water being formed, and the hydrogen thus taken out being replaced by oxygen; but it is clearly not the basic atom of hydrogen in alcohol which is thus replaced, for acetic acid retains it with its characteristic properties heightened. It is, therefore, the hydrogen of the radical which is thus replaced by oxygen, and acetic acid differs from alcohol by containing, instead of ethyle, this other radical, differing from it by having oxygen in lieu of an equivalent of hydrogen, and which may be called *oxygen-ethyle*, or *othyle*. We are thus led to consider the atom of ethyle as containing half the number of atoms which are generally ascribed to it, and as occupying in the state of vapour two volumes and not four. But I endeavoured to obtain an experimental evidence of the correctness of this conclusion, and sought it in the decomposition of the acetates by heat, by which their elements separate into acetone and carbonate. In this decomposition, the process differs according to the two views of the constitution of acetic acid; if the atom of acetate of potash be $\begin{matrix} C_4\,H_6\,O_4, \\ K_2 \end{matrix}$ acetone and carbonate are formed by the division of one atom; whereas, if the formula of the acetate be $\begin{matrix} C_2\,H_3\,O_2, \\ K \end{matrix}$ the reaction consists in a double decomposition, by which CH_3 in one atom is replaced by KO, *i. e.* methyl by peroxide of potassium, or $C_2\,H_3\,O$ replaced by CKO_2. To ascertain which of these two opposite views is the more correct, I dissolved in water equivalent weights of acetate of soda and valerate of potash, and evaporated rapidly to dryness. The mixed salts were introduced into a retort, and subjected to dry distillation, the oily distillate shaken with aqueous potash, to remove the acids which might have come over undecomposed, and after separation from the potash, distilled with the thermometer. By uniting the products of repeated distillations, a liquid was obtained, boiling with perfect regularity at 120° C., and constituting nearly two-thirds of the original distillate. This body was found to possess the composition $C_6\,H_{12}\,O$, as shewn by the following combustion with oxide of copper.

0·704 grm. of carbonic acid and 0·2935 grm. of water were the

results of the decomposition of 0·2690 grm. of the liquid; the percentage relations, as obtained by experiment and calculation, are as follows:

	Experiment.	Calculation.	Difference.
Carbon	71·38	72·00	0·62−
Hydrogen . . .	12·12	12·00	0·12+
Oxygen	16·50	16·00	0·50+

Hence the formula is, $\begin{matrix} C & H_3 \\ C_4 & H_9 \end{matrix}$ CO, or empirically, $C_6 H_{12} O$.

The same experiment was performed with various other terms of the series, and similar results obtained, the details of which I will communicate on a future occasion. On distilling equivalent parts of an acetate and formiate, the corresponding reaction would consist in the formation of a body having the composition of aldehyde, which is the hydruret of ethyle, as acetone is its methyle-compound.

The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of.

XXIII.—*On the Valuation and Composition of Protochloride of Tin.*

By Frederick Penny, Ph.D., F.C.S.

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The principal object of the present communication, is to make known a ready process for estimating the value of protochloride of tin.

This compound, it is well known, is extensively employed by dyers and printers, under the names of "crystals, or salt of tin," and "single" and "double muriate of tin;" the first is the salt in its crystallised state, and the others are solutions of it in water, with excess of hydrochloric acid. The consumption of these articles is very considerable. In Glasgow alone, the production of "crystals of tin," in the course of a year, is estimated at from 150 to 200 tons; and in

Manchester and its neighbourhood, the annual consumption is, I am informed, even greater than this, being perhaps not less than from 250 to 300 tons.

In common with other chemical products used in the Arts, these preparations of tin are of course liable to become contaminated with accidental impurities; and there is no doubt that, by some makers, they are occasionally adulterated, for the purpose of economising the tin, though the practice, I am led to believe, is rarely carried to such an extent as formerly prevailed. Metallic zinc was at one time freely added in the process of dissolving the tin in hydrochloric acid, not only as a substitute for the more expensive metal, but because it assisted, as many believed, in giving to the crystals the peculiar pearly or silky lustre for which they are usually esteemed. Besides zinc, I have discovered also the presence of minute quantities of arsenic, sulphates, common salt and muriate of magnesia.

At the present time, however, I am satisfied that the leading makers of these articles in Glasgow do not intentionally add any metallic adulteration. The principal adventitious matters contained in the crystallised chloride are water and excess of hydrochloric acid, arising from imperfect drainage of the crystals. This is particularly the case with fibrous or feathery crystals, which have the power of retaining mechanically a considerable proportion of the mother-liquor.

The value of these preparations, as respects the several purposes to which they are applied in the tinctorial arts, depends evidently on the amount of tin they contain; it being also essential that the metal should exist exclusively in the state of protochloride.

A simple process for estimating the quantity of tin in commercial samples of these articles has long been a desideratum among practical men. The common method for the determination of tin by the agency of nitric acid, is quite inapplicable to the analysis of the protochloride; as, during the necessary ebullition, a considerable proportion of bichloride is formed, which, from its ready volatility, would be expelled in the course of the subsequent evaporation, thereby involving a serious loss. Another method, which I have, by repeated trials, found capable of giving very exact results, consists in precipitating the tin by metallic zinc, and afterwards converting it into the binoxide; but these operations are much too tedious, and involve too many nice manipulations, to be available for general purposes. The process by sulphuretted hydrogen is for the same reasons even more objectionable.

Several centigrade methods have also been recommended for the

solution of the same problem. M. Cotterau* tried to estimate tin in solution of chloride of tin by colouring it with sulphate of indigo, and afterwards adding a solution of chlorine until the indigo was bleached. A somewhat similar attempt was long since made by Pelouze. Gaultier de Claubry† proposes a normal solution of iodine in alcohol for the same purpose; and for a series of experiments to be made without much time intervening, there can be no doubt that this mode will give very satisfactory results. It is, however, well known that alcoholic solutions of iodine become materially changed by keeping; and as it would therefore be necessary to test the normal liquid previous to each application, this method, is, to a certain extent, unsuitable for common use. Mène has very recently‡ suggested the employment of sesquichloride of iron for the analysis of proto-compounds of tin, and has reported very favourably of the trials he has made.

The agent which I propose to employ is bichromate of potash. Its application is based upon the fact that chromic acid, in presence of free hydrochloric acid, converts protochloride of tin into bichloride; the chromic acid becoming sesquichloride of chromium. The reaction that takes place with bichromate of potash is represented in the following equation:

$$3\,SnCl + KO.\,2\,CrO_3 + 7\,HCl = 3\,SnCl_2 + KCl + Cr_2Cl_3, + 7\,HO.$$

The operations which the present process involves are easily performed, and are precisely similar to other well-known centigrade methods of analysis. A normal solution of the bichromate is added to a known quantity of the chloride of tin dissolved in water, till on being tested with a solution of acetate of lead, a slight excess of the chrome-salt is indicated by the production of yellow chromate of lead. The amount of metallic tin is then deduced from the quantity of bichromate of potash consumed. Centigrade methods of valuation are now so extensively used, that, to scientific chemists, the necessary manipulations will at once be obvious; but as I am desirous of rendering the process available to practical men, I hope it will not be considered unnecessary to give a detailed statement of the mode of proceeding. I shall in the first place, therefore, describe the operations for estimating the value of commercial specimens of "crystals of tin;" and afterwards explain the process for testing the prepared

* J. Chim. Méd. [3], II.
† Compt. Rend. July, 1846.
‡ Compt. Rend. July, 1850.

liquors called "single muriate" and "double muriate of tin." I shall then give the results of some experiments I have made, to ascertain the true atomic composition of the crystallised protochloride.

I.—CRYSTALS OF TIN.

This salt is usually sold to the printer in jars, containing from two to three cwts. each. A fair sample, which should not be less than one or two pounds, is taken from the bulk, and triturated in a mortar until thoroughly mixed. Very frequently this operation requires considerable attention, as the crystals, in consequence of their dampness, are apt to cake under the pestle.

100 grains are then weighed out, put into a basin with 2 ounces of water and half an ounce of hydrochloric acid, and the mixture gently heated. 83·2 grains of bichromate of potash are next dissolved in about 2 ounces of tepid water, and the solution carefully transferred to an alkalimeter of 100 measures, which is filled to the top line of the graduations, by the addition of water, and then inverted on the palm of the hand for the purpose of rendering the liquid uniform throughout. This quantity of bichromate of potash, as I shall presently show, is exactly equivalent to 100 grains of pure metallic tin; and hence, each measure of the alkalimeter will be equivalent to one grain of the metal.

The alkalimeters in common use for centigrade analysis, are generally made of such a capacity, that 100 measures will contain exactly 1,000 grains of water; but for the present process, I find it much more convenient, as well as more conducive to accuracy, to have the instrument of double this capacity, so that the hundred measures will hold 2,000 grains of water.

A solution of acetate of lead, which, to avoid repetition of words, I shall call the "lead-test," is spotted over a white porcelain slab, placed conveniently for testing the tin-solution during the next operation. It should contain at least 1 ounce of the acetate to 8 ounces of water, and should be rendered clear by filtration. The spots on the slab must be pretty large, in order to ensure excess when mixed with the chloride of tin.

The prepared solution of bichromate of potash is now poured very cautiously into the tin-solution, as in the well-known process of alkalimetry, until a drop of the latter, taken out on the end of a glass rod, and applied to the "lead-test" on the slab, gives a faint yellow tinge. The operation is now finished. The number of measures of the chrome-liquor consumed is carefully read off, and this number indicates the amount of tin in 100 parts of the sample.

It may be as well to mention here, the effects produced during the foregoing operation. On the first addition of the chrome liquor to the tin-solution, sesquichloride of chromium is formed, which gives to the mixture a rich green colour; and if, at this stage of the process, a drop be applied to the lead-test, a white precipitate of chloride of lead will appear. These effects continue to be produced till all the protochloride of tin is converted into perchloride; but when this result is accomplished, and there is the smallest excess of bichromate of potash, the lead-test gives the yellow chromate of lead, simultaneously with the colourless chloride, and thus communicates the yellow shade, which indicates the completion of the process.

The question may here be raised, whether the indications afforded by a solution of acetate of lead, as applied in the present process, are sufficiently delicate to detect minute quantities of bichromate of potash; and more particularly when, as in this action, there is such an abundant formation of chloride of chromium, which by its deep green colour, appears so likely to modify, or even disguise altogether, any other tint. I have examined this point very minutely: I tried, in the first place, the sensitiveness of acetate of lead, spotted on a slab, in detecting bichromate of potash dissolved in pure water; and I found that 1 part of the chrome-salt, with 10,000 of water, gave a decidedly yellow coloration to the lead-solution; with 15,000 of water, the yellow tint was still developed, though very slightly; and with 20,000, the tinge was only just perceptible. I then added a solution of pure chloride of chromium to one of the bichromate of potash, until the mixture had a deep green colour; and after several progressive trials, I satisfied myself that the presence of 1 part of the chrome-salt, even when thus coloured, may be at once discovered in 10,000 of water.

These results are sufficient to show that for indicating excess of the chrome liquor, a strong solution of acetate of lead, though used in small drops, and in presence of chloride of chromium, is an extremely delicate test; and that it may, therefore, be with confidence relied on for ordinary practical purposes. It undoubtedly requires a little practice to be able to catch the precise moment when the yellow shade is communicated; but I have observed that individuals previously unacquainted with the manipulations of centigrade processes, have no difficulty, after two or three trials, in deciding when the operation of adding the normal chrome-solution is completed.

For the sake of convenience, I have limited the quantity of the chloride used in each operation to 100 grains; but the process

obviously possesses the advantage of being executed as easily with 500 or 1,000, as with 100 grains. In the analysis of commercial products, involving perhaps the valuation of many cwts., or even tons, the employment of large quantities is undoubtedly of essential importance; and this is more particularly the case when the processes are intended for the use of practical operators connected with chemical works.

When it is considered desirable to be very exact, I would recommend that 40 grains of bichromate of potash, dissolved in water, should be added to the tin-solution, and that the alkalimeter should be made up with only 10 grains of the chrome-salt. The remaining part of the process is conducted according to the directions previously given. By this modification, it is very easy to limit the excess of chrome-liquor to half a measure of the alkalimeter, which is equivalent to ·05 grains of the salt.

I may state, that I frequently make use of another test for detecting minute quantities of chromic acid and bichromate of potash. This consists of sulphocyanide of potassium and pure protosulphate of iron, dissolved together in water, and slightly acidified with hydrochloric acid. A white slab is spotted over with this mixture, and the solution to be tested is brought into contact with it, as when acetate of lead is used. So long as the tin-solution contains any protochloride of tin, little or no effect is observable upon the sulphocyanide mixture; but the moment the conversion into perchloride is complete, and there is the least excess of chromic acid in the solution, a dark brown or red coloration is produced. The depth of the colour depends entirely on the proportion of chromic acid present. With an extremely minute quantity, the colour is brownish; but with a great excess, the tint is blood-red. It is of no consequence if a faint pinkish tinge be developed on mixing the solution of sulphate of iron with that of the sulphocyanide, because when dropped on the slab, this slight colouration becomes scarcely appreciable. This mixture, which I shall call the "sulphocyanide-test," is an extremely delicate reagent. One part of bichromate in 10,000 is easily discoverable, even when the solution is coloured with sesquichloride of chromium; and with pure water, 1 part in 20,000 may be detected. I am inclined to give the preference to this test, because the coloration is more distinct, and more easily recognised, than the yellow tinge with acetate of lead; but as considerable nicety is required in the preparation of the sulphocyanide-test, I am afraid it will be liable to failure in the hands of inexperienced operators.

I have also used this test very successfully in the estimation of

arsenious acid by means of bichromate of potash; but I shall reserve a description of its application to this purpose for a future communication.

II.—SINGLE MURIATE AND DOUBLE MURIATE OF TIN.

In estimating the value of these preparations, I operate somewhat differently from the process described for valuing "crystals of tin." Instead of pouring the solution of bichromate of potash into that of tin, I find it more convenient to make up an alkalimeter with the tin-liquor, and to add this gradually to a known weight of the chrome-salt, dissolved in water, until the chromic acid is completely deoxidized. This result is immediately indicated when the mixture ceases to give a red coloration with the sulphocyanide-test, or when it no longer produces a yellow colour with acetate of lead. In operating according to this method, it will likewise be noticed, that the gradual changes of colour which the solution undergoes during the additions of the tin-liquor, indicate with tolerable certainty the approach of the process towards completion. So long as there remains any appreciable quantity of the chrome-salt unchanged, the solution has a yellow shade; but when deoxidation is perfect, it becomes of a rich and pure green. The necessary manipulations are as follows:

500 grains of the sample, whether "single" or "double muriate," are poured into the alkalimeter, and sufficient water added to fill the instrument to 0°, the two liquids being well mixed by agitation.

41·6 grains of bichromate of potash are dissolved in a basin, with 2 ounces of warm water and a quarter of an ounce of hydrochloric acid; and into this mixture the tin-solution is poured from the alkalimeter, in small successive portions, until, on bringing a drop of it into contact with the "sulphocyanide-test," previously spotted on a slab, no red or dark colour is seen to be produced. The number of measures consumed is read off, and on dividing 1,000 by this number, we obtain the proportion of tin in 100 parts of the sample. In a particular experiment with a specimen of "double muriate," of the specific gravity 1·600, I found that, with 500 grains in the alkalimeter, 41·6 grains of the bichromate required 35 measures, which give 28·57 per cent of tin; with a sample of "single muriate" (specific gravity 1·422), 47·5 alkalimetrical measures were consumed, equivalent to 21 per cent of tin.

Great care should be taken that the bichromate of potash employed in these processes is perfectly pure. As usually sold, it is quite

unfit for the purpose, in consequence of a large admixture of sulphate of potash; it may, however, be easily purified by two or three crystallisations; and previous to being used, it should be finely powdered, and heated to incipient fusion.

III.—QUANTITATIVE RATIO OF BICHROMATE OF POTASH AND METALLIC TIN.

In the application of centigrade processes to practical purposes in the chemical arts, it is unquestionably of the greatest importance to determine, with vigorous accuracy, the quantitative proportions of the agent of valuation, and the substance to be estimated. In the present case these are bichromate of potash and metallic tin. It is quite useless to take, as the basis of our calculations, the atomic weights usually assigned to these substances, as they are by no means satisfactorily established. I have, in another communication,* referred to the discrepancies in the numbers deduced for the metal chromium, which of course seriously involve that of bichromate of potash. The number for tin is not in a much better position. According to the well-known investigations of Berzelius, the atomic weight of this metal is 58·8, but the recent experiments of Mulder and Vlaanderen† give exactly 58. Both these numbers were obtained by converting a known weight of tin into binoxide, a method which is scarcely adapted for deciding between disputed numbers, when they correspond so closely. The following table shows the quantities of bichromate of potash required by 100 parts of metallic tin, according to the several atomic weights that have been assigned to tin and chromium, taking that of potassium at 39.

Atomic Weights of Tin.	Chromium at 26	Chromium at 26·5	Chromium at 27	Chromium at 28
58·	84·4	85·0	85·63	86·78
58·5	83·75	84·3	84·90	86·04
58·8	83·33	83·9	84·46	85·60
59·0	83·00	83·6	84·18	85·31

On examining these numbers, it will be seen that the maximum quantity of bichromate required for 100 parts of tin, is 86·78 parts, and that the minimum quantity is 83 parts, which, I apprehend, is very much beyond the reasonable limits of experimental error, when pure materials are employed.

* British Association Report, 1850.

† J. Pr. Chem. XLVIII, 31.

Rejecting, therefore, the present atomic weights, I deemed it better to have the evidence of direct experiment. I prepared some pure metallic tin from carefully purified binoxide, and dissolved a known weight of it in a flask, with strong hydrochloric acid. To the solution, diluted with water, rather less than the quantity of bichromate, which previous trials had indicated to be sufficient, was added at once, and a further quantity was then dropped from an alkalimeter (made up with only 5 grains of the salt), until the slightest appreciable effect was produced with the sulphocyanide-test. I repeated the experiment several times, varying it occasionally by adding the solution of tin to that of the chrome-salt. I also frequently used the lead-test, which gave, however, rather a higher result, as regards the proportion of bichromate consumed, than the sulphocyanide mixture, owing, as I have already explained, to the circumstance of the yellow tinge not being so easily recognised as the red shade with the latter test. The mean of all my experiments gave the ratio of 100 of tin to 83·2 of bichromate, which I feel satisfied may with confidence be taken as the basis of calculation in estimating the value of protochloride of tin. A much more extensive series of experiments would of course be required to decide the question of the atomic weights of chromium and tin; but the present results, although they have no pretension to this high character, are certainly conclusive in showing that the old numbers assigned to these metals respectively, viz., 28 and 58, cannot be correct.

IV.—COMPOSITION OF CRYSTALLISED PROTOCHLORIDE OF TIN.

All authorities seem agreed in representing the composition of crystallised protochloride of tin by the formula, Sn Cl . 3 HO. I have analysed, by different methods, numerous specimens of this salt, prepared in a variety of ways, but I have never met with it containing more than 2 HO, which undoubtedly is the atomic proportion. The mistake of assigning 3 atoms, may have arisen from the great difficulty of obtaining the crystals in a state of perfect dryness. The methods commonly employed for drying saline substances, are inapplicable to this salt, in consequence of the extreme facility with which it becomes altered, especially by heat and contact with the air; and over oil of vitriol it becomes anhydrous.

In crystallising this salt on the large scale, two sorts of crystals are generally obtained. The one sort is frequently found deposited on the sides of the moulds, or crystallising basins, and the other is usually formed in the central parts of the solution. The former are

bold, rhombic prisms, and are frequently coarse and lumpy, whence they have been mistaken for alum; the latter are exceedingly delicate and acicular, with a peculiar silky lustre, for which they are preferred. These may be obtained of great beauty by cautiously crystallising the mother-liquor from a crop of the tin-salt.

There is another variety of the crystals of this chloride, which occasionally proves troublesome to some manufacturers. It consists of extremely thin and nacreous scales, and is generally observed to form when old liquors, which have been much exposed to the air, are in process of being worked up. I shall take occasion again to refer to these crystals.

I made several attempts to purify commercial crystals of tin, by re-crystallising from distilled water, acidulated with hydrochloric acid, but the process on the small scale was very unsatisfactory, and almost impracticable. After trying other methods, I was led to adopt rather a novel mode of purification, which by a little practice, gave me the crystals both pure and dry.

In the course of my experiments upon ordinary crystals, I frequently had occasion to observe the very low temperature at which they liquefied on the application of heat; and not finding any definite statement with regard to this point, I made it the subject of particular examination. A quantity of crystals were cautiously heated in a small flask, arranged in a water-bath, with a thermometer in the water, and the bulb of another in the chloride. The experiment was commenced at 60° F., and the successive results carefully watched. At 90°, the salt began to soften, at 100° it was partially liquefied, and at 105° it became perfectly fluid. Being then allowed gradually to cool, no change was observed till the temperature had fallen to 90°, when crystallisation commenced, and the temperature rose rapidly to 105°, at which point it was for some time stationary. It afterwards slowly descended till it had again reached 90°, when congelation was perfect. I repeated this experiment several times, with very nearly the same results. The production of crystals of chloride of tin by this process is an exceedingly beautiful example of crystallisation. The fused salt does not become confusedly solid, as generally obtains with saline substances, nor is there a crust formed on the surface, if the fluid is preserved from agitation, and from the too rapid abstraction of heat by contact with the air. Large and well-defined prisms, frequently more than an inch in length, shoot in a radiating form from the sides of the vessel, and as soon as a good crop has been deposited, the remaining fluid may be poured off, and the crystals left of sufficient hardness and strength to be preserved. It is well-

known that bismuth, sulphur, and several other substances, may be crystallised by a similar process, but in these cases we have no opportunity of witnessing the actual formation of the crystals, and only see the result when the interior fluid is poured out and the crust removed. With chloride of tin, however, we can watch the very growth of the crystals, and with this advantage, that when small quantities are employed, the process may be executed in a few minutes. For practical illustration, we could not desire a more striking and ready experiment.

I availed myself of this process to purify a quantity of the chloride for analysis. The operation was repeated twice upon a considerable quantity of crystals, rejecting the fluid portion each time, and then selecting the largest and best-defined prisms.

The proportion of tin was determined in two ways: first, with the bichromate of potash, as before explained; and secondly, by dissolving 50 grains in water acidulated with sulphuric acid, and precipitating the tin with a slip of zinc. The tin was afterwards converted with the necessary precautions into binoxide, from the weight of which the metallic tin was calculated. The results obtained by these two methods agreed very closely.

For the estimation of the chlorine, 20 grains were precipitated by zinc, as in the last experiment; the solution and washings were treated with nitrate of silver, and the chlorine deduced from the chloride of silver in the usual way.

The amount of water was determined by exposing a known weight of the salt, for several hours over oil of vitriol, under the exhausted receiver of the air-pump.

The mean of several analyses gave as follows:

Tin	52·36
Chlorine	31·53
Water	16·11
	100·00

I have likewise analysed several specimens of carefully picked crystals from the centre and sides of the crystallising moulds, and also a remarkably fine sample deposited slowly from the mother-liquor. The results in every case correspond very closely with those given above, and leave no doubt whatever, that crystallised protochloride of tin contains only 2 atoms of water.

Since these analyses were completed, I find that the composition of this salt has been made the subject of investigation by

Mr. Thomas Henry,* in the course of his experiments upon the iodides of tin. His process of analysis, however, as regards the tin and chlorine, is essentially different from the one I have adopted. He determines the tin by sulphuretted hydrogen, and the chlorine by the addition of nitrate of silver to the solution, after separating the sulphuret of tin. His results are almost identically the same as mine, and clearly show that the formula for the crystals is SnCl, 2 HO. The specific gravity of the crystals is 2·710 at 60° F., and when fused, 2·5876 at 100°.

The flaky variety of the crystallised chloride, to which reference has previously been made, gave the following results:

Tin	52·2
Chlorine	30·9
Water	16·2
	99·3

It will be observed that the loss in the analysis is rather greater than seems warrantable, and that the amount of chlorine is rather less than the quantity found in the ordinary crystals. I am inclined to attribute the loss to the admixture of a small quantity of oxychloride of tin; but whatever the cause may be, it is quite clear that these crystals have the same composition as the acicular variety, being modified in form, most likely by the presence in the liquor of a small quantity of oxychloride, and perhaps bichloride. When fused by heat, and allowed to cool, they crystrallise in the usual acicular form. Thomson† has mentioned scaly crystals of chloride of tin; and he states that they consist of protochloride and perchloride, but the particulars of the analysis are not given.

The flaky crystals which I have described, are readily produced by adding to an old and concentrated solution of the protochloride an excess of hydrochloric acid, and keeping the mixture in a closed vessel for several days at a temperature of about 40°. They may be still more easily and expeditiously procured by dissolving a small quantity of old crystals in a portion of mother-liquor, and keeping the solution for a few hours, *in vacuo*, over oil of vitriol. The crystals formed in this way are sometimes from two to three inches in length, and nearly the same in breadth, but exceedingly thin and soft, and on being removed from the liquid, are reduced almost to a state of pulp.

* Philosophical Transactions, 1845, II.

† System of Chemistry, II, 822.

In conclusion, I may take the opportunity of remarking, that the facility with which "crystals of tin" melt on exposure to heat, shows the necessity of keeping the stock in a cool store, away from the fires and stoves. An absurd practice prevails at some print-works, of placing the jars containing the crystals in rooms artificially heated, so that in a very short time a part of the salt is liquefied, and collects as a sort of sludge at the bottom of the jar, entailing not only a loss of the article, and perhaps damage to the goods, but too frequently unmerited censure upon the maker. This article is well known to be one of the most delicate chemical salts used in the tinctorial arts. From its extreme liability, when damp, to change by keeping and contact with the air, it obviously requires to be used as soon as possible after it is made, and to be kept in carefully closed vessels. Its purity, perhaps, would also be much better preserved, were it sold in jars of smaller size than those in common use.

TIN-FOIL.

Another substance to which I may refer as connected with the present subject, is tin-foil. A very considerable proportion of the article sold under this name, is merely sheet lead, covered with a coating of tin. The adulteration may be easily detected by plunging the suspected foil, several times in succession, into moderately strong nitric acid. Pure tin-foil is, after a few immersions, completely converted into binoxide, which collects at the bottom of the acid; whereas impure foil, on being subjected to the same treatment, speedily loses its coating of tin, and leaves the sheet lead with its characteristic colour and appearance. The adulterated foil has likewise a higher degree of lustre than the pure article, so that, when placed side by side, they may readily be distinguished. A specimen of the impure foil gave, by analysis, in 100 parts:

Lead	65
Tin	35
	100

Many parties, no doubt, are already aware of this adulteration, but it is not, I think, generally known. Dealers in the article frequently sell the impure foil at the same price as the pure; and many have assured me that they were not previously cognisant of the fact of its being adulterated with lead.

XXIV.—*A Chemical Examination of the Metals and Alloys known to the Ancients.*

By J. Arthur Phillips, F.C.S.

Among the arts cultivated by mankind in the infancy of the world, Metallurgy appears to have held a very prominent situation; for we read that Tubal Cain was an instructor of every artificer in brass and iron,* and consequently these, together with their uses, must have been well known to the antediluvians.

It is also probable that they were not the only metals in use at this remote period; for the extraction of iron from its ores, of itself indicates great metallurgical skill and experience, as from the refractory nature of the materials employed, a very intense heat and skilful manipulation must have been necessary to its production. From these considerations we may infer that this metal could not have been discovered until the arts had attained a great degree of perfection, and long after the discovery of some others requiring less complicated apparatus and a lower temperature for their reduction. It would be quite impossible, after the lapse of so many ages, to trace the exact order in which the metals became known; but it appears natural to suppose that those which are found in a native state, were the first to attract the attention and exercise the ingenuity of mankind; and consequently, that gold, silver, and copper, were among the first with which the ancients became acquainted.† This, however, is but conjectural, as in the first mention of silver, Abraham is described as weighing unto Ephron, four hundred shekels of silver current money with the merchant,‡ thus indicating, that in those days, it was not only well known, but commonly used as a medium of exchange, for which purpose it was estimated by weight.

In the time of Moses, at least six metals were known, as in his direction for the purification of the spoils of the Midianites, he says: "Only the gold and the silver, the brass, the iron, the tin, and the lead, every thing that may abide the fire, ye shall make it pass through the fire and it shall be clean."§ Thus showing that the metallurgical

* Gen. IV, 22.

† It is true that iron is sometimes found in the native state, as large masses of meteoric origin have been occasionally met with; these, however, occur but seldom, and in quantities far too small to have supplied this metal for the uses of the arts.

‡ Gen. XXIII, 16.

§ Numbers XXXI, 22.

arts had at that period attained considerable perfection, and that the metals were of frequent occurrence and constant employment. Of the processes practised in the early ages of the world, little can at present be known; but it would appear likely, from some passages in the sacred writings, as well as from the somewhat confused and obscure accounts of profane authors, that they differed but little from those which are employed at the present day.

That silver was at a very early period purified by means of lead, the following passages would seem to indicate: "The house of Israel is to me become dross; all they are brass, and tin, and iron, and lead in the midst of the furnace, they are even the dross of silver."* And again, "The bellows are burned, the lead is consumed of the fire, the founder melteth in vain."† We also read of silver being purified in a furnace of earth. Strabo quotes Polybius as speaking of a silver ore which after being washed seven times, was melted with lead and became pure silver.

That tin was not only well known, but also highly valued at the time of the Trojan War, we learn from Homer, who calls it *κασσίτερος*, and mentions it as forming part of the armour of Agamemnon,‡ and shield of Achilles,§ to make which, Vulcan is represented as throwing into the crucible brass unconquered, *κασσίτερος*, and honoured gold and silver.

Among the ancient Greeks and Romans, the workers of metal had attained a pitch of excellence, in some instances scarcely to be surpassed in the present day; but although many proofs of their skill have come down to us, in the form of coins, statues, and implements of war, yet their authors afford but scanty information relative to the methods employed in their production. This may be accounted for by the fact, that those who have written on the subject could have been but imperfectly acquainted with it; from the circumstance of the metals being generally found and extracted in mountainous countries, at a great distance from the large and populous cities in which the authors may be supposed to have usually resided, and who were, therefore, dependent for their facts on those who might be unable to enlighten them very fully on the subject.

Is it then to be wondered at, that our stock of information should be very limited, or that the ancient authors should treat rather of the uses of the metals, and the formation of alloys, than of their extraction from the ores?

* Ezek. XXII, 18.
† Jer. VI, 29.
‡ Iliad, 2.
§ Iliad, 18.

The art of working the alloys of copper was cultivated in Rome at a very early period after the foundation of that city, as we read that King Numa, the immediate successor of Romulus, founded a fraternity of brass founders, from which it may be inferred that the trade was even then in a flourishing condition.*

At the date in which Pliny wrote his Natural History of the World, the Romans had acquired a very extensive knowledge of the metals, and their uses; as we find him, in his thirty-third and thirty-fourth Books, not only describing gold, silver, brass, tin, iron, lead, antimony, mercury and cadmia; but he gives us also the proportions in which these various metals should be mixed in order to form suitable alloys for casting, soldering, and brazing, and moreover describes with a great degree of accuracy, the medicinal and other properties of some of their oxides and salts, as well as the method of their preparation and the localities in which they were found. But his descriptions of the means used for the extraction of these metals from their ores, are not only imperfect, but also frequently very obscure. This arises both from the abrupt transitions which continually occur, and also from frequent allusions to methods and apparatus long since obsolete, and on which at the present time we have no means of acquiring any knowledge.

In speaking of gold, Pliny says,† "In these parts of the world in which we live, gold mines are found, to say nothing of India, where the ants cast it up out of the ground, or that which the griffins gather in Scythia. The gold with us is procured in three ways; among the sands of some great rivers, such as the Tagus in Spain, the Po in Italy, Hebrus in Thrace, Pactolus in Asia, and the Indian Ganges, all of which yield gold. Neither is there any gold finer or more perfect, from being thoroughly polished, by the rubbing and attrition which it meets with in the course of the streams of water. There is also another method of obtaining gold, viz. by digging it out of pits which are sunk for that purpose, or else in the caverns and breaches which occur by the fall of mountains." He also goes on to say, that the gold obtained by cleaving and opening mountains needs no trying or refining, as it is naturally fine and pure. In speaking of the value of gold, the same author remarks:‡ "The reputation which it has acquired is for the following reason, that it alone, of all things, loses nothing in the fire, but withstands its action without change. Indeed the oftener it has been in the fire the more refined and purer it becomes. One method of testing the quality of gold is by the

* Pliny, XXXIV, 1. † Pliny, XXXIII, 4.
‡ Pliny, XXXIII, 3.

application of fire, of which it ought to take not only the colour, but to a certain extent the radiance also. This kind is called *Obryzum*. This is another astonishing property of gold, that a fire made of light straw or chaff will quickly melt it, whilst if it be thrown on the strongest fire of wood-charcoal, it will with difficulty yield to its intensity and melt. With respect to its purification, it should be melted with *lead*. The second property which causes gold to be so highly valued is, that it loses but little of its weight by use and attrition, whilst silver, lead, and copper, leave metallic stains on bodies which they touch, and soil the skin of those who handle them. Neither is there any metal which can be beaten out broader by the hammer, or divided more easily into parcels, as every ounce of it may be reduced into more than seven hundred and fifty leaves, each one of which being four fingers square. The other minerals, after their extraction, require the fire for their conversion into metal, but gold, of which we now treat, is gold as soon as it is found." Again, "neither rust nor canker alters the weight of gold, or affects in any way its quality. Salt and vinegar, though such active solvents, do not make the least impression on it."

The above quotations go to show, that many of the properties of gold were known at this period, and also that the methods of extracting it from the earth, were similar to those employed at the present day. Pliny, however, gives us but little information relative to its metallurgic treatment, except that lead was employed in its purification, and also that when found in lumps it was of itself pure, and required no artificial refining. He also states, when speaking of the properties of mercury,* "So penetrating is this liquor, that there is no vessel but it will eat and pass through. It supports everything which may be thrown into it, unless it be gold only, which sinks to the bottom. It is besides, very useful for the purpose of refining gold; to effect which object, that metal mixed with cinders is placed in an earthen pot, and shaken with mercury, which rejects all the impurities mixed with it, but in return takes hold of the gold itself. To expel it from the gold, the mixture is poured on skins, which on being pressed, allow the mercury to pass through them in drops, whilst the gold remains in all its purity." The above process differs little from those in general use, for the purposes of amalgamation, at the present day, but in this case also, Pliny's description is very imperfect, inasmuch as the solid amalgam remaining on the skins would require the separation of the combined mercury before the gold could exist in the pure and fine

* Pliny, XXXIII, 6.

state described. No mention is moreover made, of any means of separating gold from silver, or in fact of their ever being found associated, except in an alloy called *electrum** said to be found in veins, and of which an artificial kind was made by mixing one part of silver and four parts of gold, and which appears to have been anciently in great request, as Homer describes the palace of King Menelaus as glittering with gold, electrum, silver, and ivory. This alloy, though sometimes made by the direct mixture of the two metals, was, doubtless, in most instances, a natural production, as many gold ores also contain a certain portion of silver, and the ancients being apparently ignorant of the method of separating them, and without any knowledge of the stronger acids,† might have been in the habit of occasionally adding a certain quantity of silver to specimens of gold which already contained a proportion of that metal, thereby converting it into electrum, in preference to allowing it to remain as impure gold.

That silver was formerly, as at the present day, chiefly extracted from the ores of lead, we are distinctly informed by the author of the "Historia Naturalis," who adds, that those ores of silver which do not contain lead or an ore of lead, cannot be successfully worked without the addition of either one or the other. Tin and lead, he seems to regard as only two varieties of the same metal, as he describes them under the title of white lead, and black, and states that the white lead called in Latin *Plumbum candidum*, and by the Greeks *Cassiteros*, was much more valuable, and commanded a higher price than the black variety.

His description of the *Plumbum candidum*, and the state in which it was found, leaves no doubt that this much-valued metal was tin, it being represented as occurring among sand, in the dried-up beds of rivers, and as only known from the other substances with which it

* Pliny, XXXIII, 4.

† Nitric acid is first mentioned by Geber, who lived in the eighth century. He describes it under the name of "dissolving water," and prepared it by distilling in a retort one pound of sulphate of iron of Cyprus, half a pound of saltpetre, and a quarter of a pound of alum of Jameni. This process, although not economical, would certainly produce nitric acid, and to this when obtained, he added sal-ammoniac, in order to give it the property of dissolving gold. Raymond Lully, who lived in the early part of the thirteenth century, employed the same process, except that he omitted the alum. Basil Valentine, who was born about the year 1400, describes a method of obtaining "Spirits of Nitre," by distilling nitrate of potash with powdered porcelain or clay, with which the potash entering into combination the same result is obtained as by the former method. Basil Valentine is also the first who describes oil of vitriol, which he prepared by distilling sulphate of iron according to the method at present practised at Nordhausen in Saxony.

was found associated, by its dark colour and great weight.* "There is likewise found in the gold mines a kind of lead-ore which they call Elutia (stream tin). The water which is let into the mines washes, and carries down with it, certain little black stones, streaked and marked with white, and as heavy as the gold itself. It is gathered with it, and they remain together in the baskets in which the gold is collected. These are not separated from it until after melting in the furnace, when the fusion transforms them into white lead." Again: "You cannot solder together two pieces of black lead without white lead, neither can this be united to the other without the aid of oil." He also says of this metal: "Neither out of the white lead can any silver be extracted; whereas out of the black this is commonly done."

In speaking of common lead, the same author says: "It is much used for conduit pipes, and for being hammered into thin plates," and then goes on to describe the mines of France, Spain and Britain, which he states, when quite worked out and exhausted, become as productive as ever, and indeed even more so, if allowed to remain a short time without being worked; for which he accounts, by supposing the metal to be produced by the air, which has then free access into the mine. With regard to the state in which *Plumbum nigrum* occurs, we are informed: "Black lead has a double origin: for it is either produced in a vein of its own without any other metal; or otherwise it is mingled with silver in the same mine, being mixed together in one stone of ore, and they are only separated by melting and refining in a furnace.† The first liquor that flows from the furnace is tin (*Stannum*), and the second silver. That part which remains behind is galena, the third element of the vein, which being again melted, after two parts of it are deducted, yields black lead."

The above passage is very obscure: tin, lead and silver are not frequently found together in the same stone, and were they thus to

* "It is generally considered that the Greeks obtained their tin by means of the Phœnicians from the Scilly Islands or Cornwall, but there is no direct proof of this; and it appears probable, from the Sanskrit derivation of the Greek word (kassiteros, from kastîra), that the Greeks originally obtained their tin from India. The Islands Cassiterides, however, the position of which was unknown to Herodotus (III, 115), are supposed to be the Scilly Islands, or the peninsula of Cornwall, though their position is not exactly defined by Strabo (III, 175). Still there can be little doubt that the Cassiterides, to which the Phœnicians from Gades (Cadiz) went for tin, and the Romans afterwards traded for the same commodity, were on the south-western angle of Great Britain."—Pen. Cyc. art. 'Hindustan.'

† Hist. Nat. XXXIV, 16.

occur, the tin certainly would not be the first to flow out of the furnace.

Professor John Phillips, in his excellent paper on "Ancient Metallurgy and Mining in Brigantia,"* seems to be of opinion that the method here described might have had some resemblance to that invented and patented by H. L. Pattinson, Esq. This, however, appears less probable when we consider that if, in Pattinson's process, the rich lead were run off, instead of dipping out the poor in the form of crystals, the metal thus obtained being but sparingly mixed with silver, would not have been called stannum, by which term an alloy of tin and lead is frequently expressed. It, therefore, does not seem impossible that the operation referred to was simply cupellation, in which process the "*abstrichs*" and first litharge flowing from the furnace is much more impure than that subsequently obtained, and, therefore, when reduced, would yield a harder lead, not unlike pewter or *Stannum*. The silver thus obtained would of course remain on the cupel, whilst the litharge which flowed from the furnace after it got into steady action, together with that absorbed by the cupel itself, would, on being melted with a reducing-agent, yield pure, or nearly pure lead. I think, therefore, the author intends to convey the idea that three parts of litharge and "*débris de coupelle*" yield only one part of lead.

That cupellation has long been employed for the extraction of silver from lead may be inferred from the works of Agricola,† who in his "De Re Metallica," describes and gives drawings of the furnaces used in his time for that purpose, and which exactly correspond in every respect with the old German cupels in use at the present day in many parts of the continent.

The Greeks and Romans have left no treatises relative to chemistry or metallurgy; but it is scarcely reasonable to suppose, that had the method of refining lead by crystallization been known to them, it should either have been lost or fallen into disuse, as its advantages are too obvious not to have been evident to the rudest operators. Another argument against the opinion of Pliny having referred to this method, is the fact that rich lead, and not pure silver as described by him, is obtained by the crystallizing process, and if this method were ever known, it must evidently have fallen into disuse before the time of Agricola, who makes no mention of any knowledge on the subject, but gives the old German furnace as that

* Proceedings of the Yorkshire Philosophical Society for March, 1848.

† Born A.D. 1494.

ordinarily employed for the extraction of silver, and which, from the circumstance of its having remained unchanged in every respect since the days of Agricola, may be inferred to have existed in the same form long prior to that time; and to have been probably not only used by the Greeks and Romans, but possibly even at a much earlier date.

Of all the metals employed by the ancients for the manufacture of objects of luxury, as well as for those adapted to the everyday usages of life, copper and its alloys were the most common; as by far the greater portion of the coins, tools and implements of war, which are occasionally brought to light, are composed of some modification of either bronze or brass; and consequently, the making of these alloys, and their adaptation to the various wants of mankind, must have formed a very important branch of the manufactures among the Greeks and Romans. Accordingly, the author of the "Natural History of the World," after describing the properties of this metal, and stating the localities in which that of the best quality was found, gives the composition and proportions employed in the various alloys then common in Rome, and informs us to what uses they were severally applied. He also states that copper was first found in the Island of Cyprus, from whence two distinct kinds were exported:* one called *Coronarium*, which when reduced into thin leaves and coloured with the gall of an ox, had a golden colour, and was employed for making coronets and tinsel ornaments for actors, from which circumstance it derived its appellation. Another variety, which was named *Regulaire*, is not particularly described, except that, like the former, it would stand hammering, and might be thus made to take any required form. The brass (copper) of the next best quality came from Campania, where it was the custom to add eight parts of lead to every 100 pounds of copper. It is also mentioned, that in France it was usual to melt copper among red-hot stones, for the purpose of obtaining a steady heat, as a quick fire was found to blacken the metal and render it brittle. He moreover informs us that the process was completed in one operation, but states that the quality would be improved by more frequent melting: "Moreover, it may not be amiss to state also, that all kinds of brass melt best in the coldest weather. For statues and tables brass is worked in the following manner: First the ore, or stone as it comes out of the mine, is melted, and as soon as this is done, they add to it a third part of scrap brass, consisting of broken pieces of vessels that have been

* Pliny, XXXIV, 8.

used; for it is time and use alone that bring brass to perfection, it is the rubbing which conquers the natural harshness of the metal. They then mix twelve pounds and a half of tin to every hundred pounds weight of the aforesaid melted ore. The softest alloy is called *Formall*, in which are incorporated a tenth of black lead, and one twentieth part of argentine lead; it is this mixture which best takes the colour called grecanic. The last alloy is that which is called *Ollaria*, or pot-brass, as it takes its name from the vessels for which it is mostly employed, and this is made by tempering every hundred pounds weight of brass with three or four pounds weight of argentine lead or tin."*

The alloys above described are merely modifications of bell-metal or bronze; but it is not improbable that the ancients were acquainted with zinc-brass long before this period. Aristotle tells us that the Mosynæci, a people who inhabited a country not far from the Euxine Sea, were said to make their copper of a splendid white colour, not by the addition of tin, but by mixing and cementing it with an earth found in that country.† We are also informed by Strabo, that in the neighbourhood of Andêra, a city of Phrygia, a remarkable kind of stone was met with, which being calcined became iron, and on being fluxed with a certain kind of earth, yielded drops of a silvery-looking metal, which when mixed with copper, formed an alloy called *Aurichalcum*.‡

Sextus Pompeius Festus, who abridged a work of Verrius Flaccus, a grammarian of considerable note in the time of Augustus, mentions cadmia, which he defines as an earth thrown upon copper, in order to convert it into aurichalcum.§

On this subject Pliny affords us but little information, merely stating where cadmia was found, and naming some of its medicinal properties, but he seems to have regarded it rather as an earth which gave a yellow colour to copper, than as the ore of a distinct metal, zinc being in no instance mentioned by him, although he speaks of a kind of brass which was manufactured in the Island of Cyprus from copper and cadmia.

If the foregoing quotations were not sufficient to show that the ancients were acquainted with the art of making zinc-brass, the fact has been fully proved by the analyses given in a subsequent part of this paper, by consulting which, zinc will be found to occur some

* Pliny, XXXIV, 9.

† Arist. de Mirab. Op. II, 721.

‡ Strabo, Geo. LXIII.

§ "Cadmia terra quæ in æs conjicitur ut fiat aurichalcum."—Fes. de ver. seq.

time previous to the Christian era, although at what precise period, it would be impossible to determine, without multiplying experiments to an unreasonable extent. That metallic zinc, however, was known to the ancients, there is no evidence to prove, since the metal mentioned by Strabo as given out in drops from a certain stone when heated, could scarcely have been zinc, which would, to a great extent, have been volatilized if treated in the way described, and we may therefore suppose, that if the stone referred to by him was an ore of zinc, it might also have contained some other metal, such as lead, with which it is often found associated, and which would produce the appearance in question. Ambrose, Bishop of Milan, describes the transformation of copper into aurichalcum as being effected by means of a drug,* and not by the addition of another metal, from which we may infer he was unacquainted with the metallic nature of the material employed, although from his calling it a drug, he was perhaps aware of its medicinal properties.

A similar description of the manufacture of brass is given by Primasius, Bishop of Andrumetum, in Africa, in the sixth century, and by Isidorus, Bishop of Seville, in the seventh. Agricola, who wrote in the sixteenth century, was also evidently ignorant that cadmia contained zinc, of which we have no authentic account until we find it mentioned by Paracelsus; and from which it is evident, that although the manufacture of zinc-brass is of great antiquity, the extraction of the metal itself is comparatively a modern discovery.

Iron, the last of the six metals known to the ancients, was not, in the earliest times, very extensively employed, as the primitive heroes are described as being armed with weapons of brass.

Pisander is represented as attacking Agamemnon with a pole-axe, of which Homer says:

> "An olive's cloudy grain the handle made
> Distinct with studs, and *brazen* was the blade."†

Plutarch informs us that when Cimon, the son of Miltiades, conveyed the bones of Theseus from the Island of Scyros to Athens, he found interred with him, a bronze sword and a spear-head of the same metal.‡

Although generally used, however, brass was not universally employed for the manufacture of arms, as the celebrated robber, Periphetes, slain by Theseus, was named Korunetes (Κορυνήτης) from

* Amb. in Apoc. CI.
† Iliad, V, 612, Pope's Trans.
‡ Theseo.

using an iron club, and Areïthous is described by the author of the Iliad as:*

> "Great Areïthous, known from shore to shore,
> By the huge knotted *iron* mace he bore;
> No lance he shook, nor bent the twanging bow;
> But broke with this the battle of the foe."

In the days of Herodotus iron must have already come into general use, as when his interpreter reads to him an inscription on one of the Egyptian Pyramids relative to the amount of money expended on radishes, onions and garlic for the workmen employed in its construction, he makes the reflection, that if this were true, how much more must have been paid for *iron tools* and bread!†

It would again seem almost incredible that these stupendous structures could themselves have been erected without the aid of steel, both for quarrying and shaping the stone, as well as for cutting the hieroglyphics so common in the earliest specimens of Egyptian architecture. If then, we allow that iron tools were employed in building these monuments, we must suppose this metal to have been in common use during the reign of the shepherd kings who conquered Egypt and occupied the throne of the Pharaohs during some part of the interval which elapsed between the birth of Abraham and the captivity of Joseph.‡

In speaking of iron, Pliny says:§ "After copper, comes iron, both the most useful and most fatal instrument of life. With iron man delves the earth, plants trees, prunes his orchards, trims his vines, cutting off the older branches, and thereby throwing more vigour into the grapes; by its aid man builds houses, cuts stone, and prepares a thousand other implements; but by it war, atrocity and villany is effected and rendered common." He also describes iron as occurring in almost every part of the known world, but particularly in the Island of Elba, where the colour of the earth indicated the presence of the ore.

We are moreover informed that the ores of iron should be treated like those of copper, in order to extract the metal, and that it was a disputed point in Cappadocia, whether the principle of iron was aqueous or earthy in its nature, as the water of a certain river of that country, when thrown on the earth, produced iron, precisely similar to that obtained from a furnace. He then goes on to say, that there are two distinct kinds of forges, as some produce steel (*nucleus ferri*), which is best adapted for cutting-instruments; whilst others,

* Iliad, V. 136, Pope's Trans.
† Herod. Euterpe, II, 125.
‡ Russell's Egypt, 89.
§ Pliny, XXXIII, 14.

shape it into instruments of common use, such as hammers and anvils; but that seasoning is the most important and delicate part of the operation. "It is a remarkable fact that, in the treatment of this mineral, the metal in melting is at first as liquid as the most limpid water, but becomes spongy in getting cold."*

From the extracts already quoted, it will be seen that the information which has come down to us relative to the metallurgy of the early ages, is both vague and to some extent uncertain; as those who describe the materials and methods employed, have themselves acquired their information from others, and were, therefore, more subject to commit errors, than if practically acquainted with the subjects of which they treated. This circumstance has induced me to believe, that a careful analytical examination of such productions of the early metallurgists, as have been discovered in different localities, would not be without interest, and I have therefore undertaken the following series of analyses.

From the advantage afforded for ascertaining dates, most of the analyses have been executed on coins, care being first taken to well establish their authenticity.

Some Celts and sword-blades have also been examined, and of these figures are given.

The analyses are placed consecutively, according to the supposed dates of the specimens examined, and the methods employed in their execution will be found fully described in the Appendix.

ANALYSES OF ANCIENT ALLOYS.

A.

COINS STRUCK PRIOR TO THE CHRISTIAN ERA.

Commerce in remote antiquity, was carried on by means of the mere exchange of commodities; and it is remarkable, that throughout the more ancient books of Scripture, as well as in the poems of Homer, no passage occurs from which it can be inferred, that stamped money was then in circulation, although mention is repeatedly made of purchases being effected through the medium of the metals, which, for that purpose, were estimated by the balance. Herodotus (I, 94) speaks of the Lydians as the first who coined gold and silver into

* Iron in Pliny's time was doubtless made by the direct, or Catalan process, and the spongy appearance above described must have arisen, not from its cooling, as he seems to suppose, but from combustion of the combined carbon, and the consequent conversion of the compound into malleable iron.

money. The Parian chronicle, however, ascribes the origin of coined money to the Æginetans, under Phidon, King of Argos, who reigned 895 years before the Christian era.* Ælian, in his "Various History," corroborates this statement, and the most competent numismatic authorities agree in considering the coins of Ægina as the most ancient specimens of stamped money which have come down to us. These are of silver, and bear on the upper side the figure of a turtle, and on the reverse an indented mark, as if the metal at the time of striking had been held on a puncheon, which, from the force of the blow, appears to have left a deep impression.

The coins of Lydia would seem to come next in point of antiquity, and after them, the early Darics of the Persian kings, which occur in both silver and gold. Pinkerton observes, "the first Grecian copper coins with which we are acquainted, were those of Gelo, King of Syracuse, about 490 years before the birth of Christ. These were called *Chalci*, or pieces of brass; others of a smaller size, were denominated *Lepta*, or *Kerma*, from being change for the poor." He is also of opinion, that the Greeks had no gold coinage before the time of Philip of Macedon, and that Athens had no gold money before the Peloponnesian war.†

The first Roman coinage was of brass, and is said to have taken place under Servius Tullius, about five centuries before the Christian era, and seems to have been confined to the *as* or *æs*, which on one side bore the two-faced head of Janus, and on the other the prow of a ship, a symbol always attending Janus, because he arrived in Italy by sea.

Varro,‡ however, informs us, that the first Roman coins bore the stamp of a bull, ram, or some other cattle, and it is therefore probable that the *As* with the head of Janus, was not the very first design issued from the Roman mint.

However this may be, soon after the first coinage of brass, the parts of the *As* of a value proportionate to their weight were also produced.§ The *Semis*, or half *As*, marked S., had commonly the head of Jupiter laureated; the *Triens*, or third, marked 0000, as being originally

* This chronicle, as it is called, consists of a series of Greek inscriptions cut in Parian marble. It was discovered in the beginning of the seventeenth century in the island of Pharos, one of the Cyclades, and was bought and brought to England by the celebrated Thomas Earl of Arundel. It is proved by internal evidence that this chronicle was engraved 264 years before the birth of Christ, most likely for Athens.

† Pinkerton on Medals, I, 77.

‡ Varro de Re. Rust, I, 2.

§ Pinkerton on Medals, I, 101.

four ounces, had the head of Minerva; the *Quadrans*, or quarter, 000, the head of Hercules, wrapt in a lion's skin; the *Sextans*, or sixth, 00, that of Mercury with a cap and wings; and finally the *Unica*, marked 0, had the head of Rome.

All the above coins were cast, as were also those of the Etruscans, from whom the Romans learnt the art of moulding their money; and that several were usually obtained at each melting, is evident from the fact that three or four have occasionally been found joined by runners of the metal of which they are made. Most of the specimens also retain the marks produced, by cutting off these threads, as likewise the lines indicating the division of the two parts of which the mould was composed.

ROMAN *AS* OR *ÆS.* B.C. 500.*

Weight, 4150 grains. Specific gravity, 8·59.
Obverse: The head of Janus. Reverse: A ship.

The metal of which it was composed, presented an iron-grey appearance when broken, but if cut, the peculiar hue of copper was immediately perceived. Large cavities were also observed in the substance of the alloy, occasioned by bubbles of air, which being shut up in the mould, had caused numerous holes in the casting.

1°. 21·80 grs. gave 18·99 grs. of oxide of copper = 69·51 per cent of copper.
1·97 grs. of peroxide of tin = 7·10 per cent of tin.
7·04 grs. of sulphate of lead = 22·02 per cent of lead.
·15 grs. of peroxide of iron = ·48 per cent of iron.
·13 grs. of metallic cobalt = ·59 per cent of cobalt.

2°. 25·42 grs. gave 22·26 grs. of oxide of copper = 69·87 per cent of copper.
2·34 grs. of peroxide of tin = 7·23 per cent of tin.
8·06 grs. of sulphate of lead = 21·62 per cent of lead.
·17 grs. of peroxide of iron = ·46 per cent of iron.
·14 grs. of metallic cobalt = ·55 per cent of cobalt.

* M. Le Normand considers the Roman As of this type, to have been coined about B.C. 385. Other authors, however, regard the date above given, as being more correct.

	I.	II.
Copper . .	69·51	69·87
Tin . . .	7·10	7·23
Lead . . .	22·02	21·62
Iron . . .	·48	·46
Cobalt . . .	·59	·55
Nickel and Sulphur	traces	traces
	99·70	99·73

SEMIS.

Same date as the foregoing.

This coin bears on one side the head of Jupiter laureated, and on the other the letter S. Its weight, although not quite perfect, was 1997 grains. Specific gravity, 8·64.

1°. 37·10 grs. gave 15·96 grs. of sulphate of lead = 29·35 per cent of lead.
28·84 grs. of oxide of copper = 62·05 per cent of copper.
3·60 grs. of oxide of tin = 7·62 per cent of tin.
·085 grs. of cobalt = 0·23 per cent of cobalt.
·09 grs. of oxide of nickel = ·19 per cent of nickel.
·10 grs. of oxide of iron = ·17 per cent of iron.

2°. 25·4 grs. gave 19·76 grs. of oxide of copper = 62·04 per cent of copper.
10·90 grs. of sulphate of lead = 29·29 per cent of lead.
2·50 grs. of oxide of tin = 7·71 per cent of tin.
·058 grs. of cobalt = ·23 per cent of cobalt.
·07 grs. of oxide of nickel = ·19 per cent of nickel.
·07 grs. of oxide of iron = ·19 per cent of iron.

	I.	II.
Copper . .	62·05	62·04
Lead . . .	29·35	29·29
Tin . . .	7·62	7·71
Cobalt . . .	0·23	0·23
Nickel . . .	·19	0·19
Iron . . .	·17	0·19
Sulphur . .	trace	trace
	99·61	99·65

QUADRANS.

This is supposed to be of the same date as the preceding, being of similar rude workmanship and brittle metal. The specimen examined bore on one side the head of Hercules, and on the other a design in which the marks 000 were conspicuous. Its weight was 970 grains; its specific gravity, 8·58.

1°. 23·43 grs. gave 21·20 grs. of oxide of copper = 72·17 per cent of copper.
2·14 grs. of oxide of tin = 7·17 per cent of tin.
6·70 grs. of sulphate of lead = 19·52 per cent of lead.
0·15 grs. of peroxide of iron = ·41 per cent of iron.
0·07 grs. of cobalt = ·29 per cent of cobalt.
·06 grs. of oxide of nickel = ·20 per cent of nickel.

2°. 25·50 grs. gave 23·10 grs. of oxide of copper = 72·27 per cent of copper.
2·33 grs. of oxide of tin = 7·18 per cent of tin.
7·32 grs. of sulphate of lead = 19·60 per cent of lead.
·13 grs. of peroxide of iron = ·36 per cent of iron.
·07 grs. of cobalt = ·28 per cent of cobalt.
·07 grs. of oxide of nickel = ·21 per cent of nickel.

	I.	II.
Copper . .	72·17	72·27
Tin . . .	7·17	7·18
Lead . . .	19·52	19·60
Iron . . .	·41	·36
Cobalt . . .	·29	·28
Nickel . . .	·20	·21
Sulphur . .	trace	trace
	99·76	99·90

HIERO I. B.C. 478.

Hiero I. succeeded his brother Gelo as King of Syracuse, 478 years before our era, and reigned eleven years.

The coin examined was of a yellow colour, and the metal bright and close in its grain, being extremely hard and difficult to cut. Specific gravity, 8·72.

1°. 22·16 grs. gave 26·18 grs. of oxide of copper = 94·26 per cent of copper.
1·55 grs. of oxide of tin = 5·49 per cent of tin.
·10 grs. of peroxide of iron = ·31 per cent of iron.

2°. 15·13 grs. gave 17·83 grs. of oxide of copper = 94·05 per cent of copper.
1·06 grs. of oxide of tin = 5·50 per cent of tin.
·07 grs. of peroxide of iron = ·33 per cent of iron.

	I.	II.
Copper . .	94·26	94·05
Tin . . .	5·49	5·50
Iron . . .	·31	·33
	100·06	99·88

ALEXANDER THE GREAT. About B.C. 335.

This coin weighed 108 grains, and the metal of which it was composed had a specific gravity of 8·69.

1°. 26·6 grs. gave 28·90 grs. of oxide of copper = 86·729 per cent of copper.
4·45 grs. of oxide of tin = 13·146 per cent of tin.
23·0 grs. gave 0·13 grs. of sulphate of baryta = ·071 per cent of sulphur.

2°. 23·81 grs. gave 25·91 grs. of oxide of copper = 86·839 per cent of copper.
3·89 grs. of oxide of tin = 12·839 per cent of tin.
23·70 grs. gave 0·13 grs. of sulphate of baryta = ·065 per cent of sulphur.

	I.	II.
Copper . .	86·729	86·839
Tin . . .	13·146	12·839
Sulphur . .	·071	·065
	99·946	99·743

PHILIPPUS III.

Natural son of Philip II. and half brother of Alexander, whom he succeeded as King of Macedonia, in the year 323 before our era.

The coin examined weighed 83·3 grains, and bore on one side a head, and on the other a man on horseback. This metal resembled that of which the coin of Alexander was composed, and had a specific gravity = 8·71.

1°. 23·40 grs. gave 26·50 grs. of oxide of copper = 90·34 per cent of copper.
2·80 grs. of oxide of tin = 9·40 per cent of tin.

2°. 15·63 grs. gave 17·68 grs. of oxide of copper = 90·21 per cent of copper.
1·89 grs. of oxide of tin = 9·46 per cent of tin.

	I.	II.
Copper . .	90·34	90·21
Tin . . .	9·40	9·46
	99·74	99·67

PHILIPPUS V. B.C. 200.

Weight about 164 grains. Specific gravity = 8·59.

1°. 19·96 grs. gave 21·30 grs. of oxide of copper = 85·15 per cent of copper.
2·82 grs. of oxide of tin = 11·10 per cent of tin.
·84 grs. of sulphate of lead = 2·87 per cent of lead.
·13 grs. of peroxide of iron = 0·45 per cent of iron.

2°. 8·89 grs. gave 9·50 grs. of oxide of copper = 85·16 per cent of copper.
1·26 grs. of oxide of tin = 11·14 per cent of tin.
·37 grs. of sulphate of lead = 2·83 per cent of lead.
·05 grs. of peroxide of iron = 0·39 per cent of iron.

	I.	II.
Copper . . .	85·15	85·16
Tin . . .	11·10	11·14
Lead . . .	2·87	2·83
Iron . . .	0·45	0·39
Sulphur . . .	trace	trace
	99·57	99·52

COPPER COIN OF ATHENS.

Weight = 89·5 grs. Specific gravity = 8·61.

Obverse: Head of Minerva. Reverse: A naked figure, represented in the act of hurling a thunderbolt. Metal, very hard.

1°. 21·0 grs. gave 23·26 grs. of oxide of copper = 88·41 per cent of copper.
2·66 grs. of oxide of tin = 9·95 per cent of tin.
·21 grs. of sulphate of lead = ·68 per cent of lead.
·08 grs. of peroxide of iron = ·26 per cent of iron.
·18 grs. of oxides of nickel and cobalt = ·67 per cent of metal.*

2°. 18·38 grs. gave 20·34 grs. of oxide of copper = 88·34 per cent of copper.
2·33 grs. of oxide of tin = 9·96 per cent of tin.
·16 grs. of sulphate of lead = ·59 per cent of lead.
·07 grs. of peroxide of iron = ·26 per cent of iron.
·15 grs. of oxides of nickel and cobalt = ·63 per cent of metal.

	I.	II.
Copper . . .	88·41	88·34
Tin . . .	9·95	9·96
Lead . . .	·68	·59
Iron . . .	·26	·26
Nickel and cobalt .	·67	·63
	99·97	99·78

EGYPTIAN. PTOLEMY IX. About B.C. 70.

AULETES (THE FLUTE PLAYER).

This coin was made of a very brittle metal, and weighed 337 grs. On one side it bore the impression of a bearded head, and on the other an eagle holding a thunderbolt. Specific gravity = 8·81.

1°. 17·34 grs. gave 18·30 grs. of oxide of copper = 84·21 per cent of copper.
3·44 grs. of oxide of tin = 15·59 per cent of tin.

2°. 13·66 grs. gave 2·73 grs. of oxide of tin = 15·70 per cent of tin.
Oxide of copper lost.

	I.	II.
Copper	84·21	84·30
Tin	15·59	15·70
Iron, cobalt and sulphur .	traces	traces
	99·80	100·00

* In this instance, the quantity of the mixed oxides being small, no attempt was made to separate them, and as their equivalent is nearly the same, the amount of the two metals together was calculated directly from the weight of the oxides found.

POMPEY. FIRST BRASS. B.C. 53.

Weight 309 grs. Specific gravity 8·70.

Obverse: Head of Janus. Reverse: Prow of a ship.

This coin was evidently cast, and the metal is very hard and brittle, resembling in this respect the alloy employed in the original *as*, before its reduction in weight.

1°. 19·93 grs. gave 18·51 grs. of oxide of copper = 74·11 per cent of copper.
2·17 grs. of oxide of tin = 8·56 per cent of tin.
4·7 grs. of sulphate of lead = 16·08 per cent of lead.
·09 grs. of peroxide of iron = ·31 per cent of iron.

2°. 18·90 grs. gave 17·58 grs. of oxide of copper = 74·23 per cent of copper.
2·03 grs. of oxide of tin = 8·38 per cent of tin.
4·50 grs. of sulphate of lead = 16·23 per cent of lead.
·07 grs. of peroxide of iron = ·26 per cent of iron.

	I.	II.
Copper . . .	74·11	74·23
Tin . . .	8·56	8·38
Lead . . .	16·08	16·23
Iron . . .	·31	·26
	99·06	99·10

COIN OF THE ATILIA FAMILY. B.C. 45.

This coin bears, on one side, the head of Janus; and on the other, the prow of a ship, with the word ROMA beneath it. The metal is extremely hard and brittle, but has been struck with a die.

Weight = 466 grs. Specific gravity = 9·02.

1°. 30·10 grs. gave 25·92 grs. of oxide of copper = 68·72 per cent of copper.
1·80 grs. of oxide of tin = 4·77 per cent of tin.
11·22 grs. of sulphate of lead = 25·42 per cent of lead.
·06 grs. of peroxide of iron = ·13 per cent of iron.

2°. 28·52 grs. gave 24·54 grs. of oxide of copper = 68·66 per cent of copper.
1·77 grs. of oxide of tin = 4·95 per cent of tin.
10·64 grs. of sulphate of lead = 25·44 per cent of lead.
·04 grs. of peroxide of iron = ·09 per cent of iron.

	I.	II.
Copper . . .	68·72	68·66
Tin . . .	4·77	4·95
Lead . . .	25·42	25·44
Iron . . .	·13	·09
Cobalt and nickel .	traces	traces
	99·04	99·14

JULIUS AND AUGUSTUS. About B.C. 42.

Weight 342 grains. Specific gravity 8·64.

1°. 21·04 grs. gave 20·80 grs. of oxide of copper = 78·88 per cent of copper.
2·13 grs. of oxide of tin = 7·95 per cent of tin.
3·95 grs. of sulphate of lead = 12·80 per cent of lead.

2°. 17·56 grs. gave 17·39 grs. of oxide of copper = 79·39 per cent of copper.
1·80 grs. of oxide of tin = 8·05 per cent of tin.
3·30 grs. of sulphate of lead = 12·81 per cent of lead.

	I.	II.
Copper . . .	78·88	79·39
Tin . . .	7·95	8·05
Lead . . .	12·80	12·81
Iron and sulphur .	traces	traces
	99·63	100·25

AUGUSTUS AND AGRIPPA. B.C. 30.

CONQUEST OF EGYPT.

Weight 238 grs. Specific gravity = 8·65.

This coin bears two heads on one side; and on the other, a crocodile, with COL: NEM. Metal very hard and brittle.

1°. 25·26 grs. gave 24·90 grs. of oxide of copper = 78·58 per cent of copper.
4·15 grs. of oxide of tin = 12·91 per cent of tin.
3·16 grs. of sulphate of lead = 8·53 per cent of lead.

2°. 17·93 grs. gave 17·60 grs. of oxide of copper = 78·33 per cent of copper.
2·97 grs. of oxide of tin = 13·01 per cent of tin.
2·29 grs. of sulphate of lead = 8·71 per cent of lead.

	I.	II.
Copper . . .	78·58	78·33
Tin . . .	12·91	13·01
Lead . . .	8·53	8·71
Iron and sulphur .	traces	traces
	100·02	100·05

LARGE BRASS OF THE CASSIA FAMILY. About B.C. 20.

Weight 365 grains. Specific gravity = 8·52.

Metal of a yellow colour, and softer than any of the foregoing.

1°. 15·73 grs. gave 16·27 grs. of oxide of copper = 82·47 per cent of copper.
3·37 grs. of oxide of zinc = 17·16 per cent of zinc.
·08 grs. of peroxide of iron = ·35 per cent of iron.

2°. 16·243 grs. gave 16·70 grs. of oxide of copper = 82·06 per cent of copper.
3·54 grs. of oxide of zinc = 17·46 per cent of zinc.
·35 grs. of peroxide of iron = ·36 per cent of iron.

	I.	II.
Copper . . .	82·47	82·06
Zinc . . .	17·16	17·46
Iron . . .	·35	·36
Sulphur . .	faint trace	faint trace
	99·98	99·88

B.

ANALYSES OF ANCIENT ARMS AND CUTTING INSTRUMENTS.

It would be impossible to determine the dates of these relics of former times with the same accuracy with which we may ascertain the ages of coins; and I shall therefore merely give the weight and dimensions of the various specimens which have been examined, and endeavour to adduce such evidence as may show their great antiquity, without attempting to specify the precise dates at which they were employed. The ancient authors who have written on this

subject, all agree that brass was used for the manufacture of arms before the discovery of iron. Lucretius says:*

> "Arma antiqua manus, ungues, dentesque fuerunt,
> Et lapides, et item silvarum fragmina rami,
> Et flammæ, atque ignes, postquam sunt cognita primum
> Posterius ferri vis est ærisque reperta
> Sed prius æris erat quam ferri cognitus usus."

Hesiod also informs us that, "In remote ages, the earth was worked by brass, because iron had not been discovered." The Etrurians were acquainted with the use of copper, and appear to have used it for the purposes of agriculture at a very early period, as when the boundaries of their city were marked out, it was done with a ploughshare of bronze.† Numerous other authorities might, if necessary, be quoted in support of the above statements; but the opening of divers Scandinavian tumuli, of very remote antiquity, in Denmark, fully establishes the accuracy of these accounts. From these barrows have been collected specimens of swords, daggers, knives, and implements of industry, since preserved and arranged in the Museum of Copenhagen, and among them are instruments of flint, resembling in their shapes, our wedges, axes, chisels, hammers, and knives; which we may infer, from their rude workmanship, as well as from the materials of which they are formed, to have been the first description of edge-tools used by mankind for the several purposes for which they were adapted. Specimens of swords, daggers and knives were also found, of which the blades are made of gold, whilst the cutting edges only are of iron. Some of these objects are composed principally of copper, with edges of iron; and in the whole of them, the profuse application of copper and gold, in comparison with the parsimony evident in the expenditure of iron, seems to prove that at that early, though unknown period, both gold and copper were more plentiful, and less highly valued than iron, among the now-forgotten people who manufactured these implements.‡

Although we have the best evidence for believing that copper and bronze were employed for the purpose of making cutting instruments before the discovery of iron, it would be more difficult to ascertain at what date and among what nation this metal first came into general use. That it was known at a very early period we learn from various passages in the Books of Moses; and that it was used in the days of Job (about B.C. 1400) for the manufacture of arms, is evident from

* Lib. I, 1282.

† Macrob. Saturn. V, 19.

‡ Jacob on the Precious Metals, I, 3.

the following passage: "He shall flee from the iron weapon and the bow of steel shall strike him through."*

It is nevertheless probable that bronze might have been in common use long after the discovery of the harder metal, as the preparation of iron must have been a very tedious and expensive operation, to a people having but a scanty knowledge of the metallurgic arts, and we accordingly find a kind of compromise between its known utility and high commercial value in the case above-quoted, in which the cutting edge alone is made of steel. At the present day, a valuable discovery made in any part of the world would speedily become known and appreciated throughout its whole extent, but at the remote time in which iron was first reduced from its ore, so little communication existed between the various nations, that that which might be well known and highly valued by the inhabitants of one country or state, might be quite unheard of in another, and consequently the uses of this metal may for a long time have been limited to a few districts where accident, or the smelting of some other mineral, had first revealed its presence. In the earliest ages of recorded history, when the world was divided into numerous petty states and principalities, the constant feuds, which were the principal occupation of mankind, would certainly cause a demand for arms and weapons of defence. Such a state of things must, however, operate most unfavourably on the cultivation of the arts; and it is not reasonable to suppose that a conquering army on entering a foreign territory would have sufficient leisure to acquire the arts of the conquered nation, and consequently, although they might find the arms of their enemies superior to their own, they would still be ignorant of the means by which they were manufactured; and thus the secret would remain for a long period in the possession of its first discoverers. At what precise epoch weapons of iron came into general use among the Romans, we have not sufficient information to decide, but in the time of Augustus,† iron mines were worked to a considerable extent in the Noric Alps (now Illyria), and from them iron of the first quality was obtained. This was used for making the best weapons, and hence "Noricus ensis," was as much synonymous for a good sword, as a Toledo, or Andrea Ferrara blade in more modern times.‡ In this sense it is used by Horace, Book I, Ode XVI, v. 9. At the time in which Pliny wrote his "Historia Naturalis," iron was almost universally employed, not only for the blades of swords, but also for the manufacture of the different cutting instruments used for

* Job, XX, 24.

† B.C. 30.

‡ Jacob on the Precious Metals, I, 88.

the purposes of daily life, as he both describes the metal and the means of forging it, and also refers to the difficulty of tempering steel in order to give it the requisite degree of hardness.

From these considerations, it is evident that the various weapons of bronze must be of great antiquity, since iron was in common use prior to the Christian era, and I have therefore placed the analyses of these instruments, in a part of the series which corresponds to that period, notwithstanding that in all probability some of them may belong to a much earlier date.

SWORD-BLADE, (FIG. 1.)

Found under Chertsey Bridge, Thames. Weight, 1 lb.; length, 17 inches; breadth at widest part, $1\frac{3}{4}$ inches; breadth where broken, $1\frac{1}{8}$ inches.

1°. 35·2 grs. gave 39·70 grs. of oxide of copper = 90·00 per cent of copper.
4·28 grs. of oxide of tin = 9·54 per cent of tin.
·17 grs. of peroxide of iron = ·33 per cent of iron.

2°. 35·8 grs. gave 40·10 grs. of oxide of copper = 89·38 per cent of copper.
4·40 grs. of oxide of tin = 9·63 per cent of tin.
·17 grs. of peroxide of iron = ·33 per cent of iron.

	I.	II.
Copper . .	90·00	89·38
Tin . . .	9·54	9·63
Iron . . .	·33	·33
Sulphur . .	trace	trace
	99·87	99·34

BROKEN SWORD-BLADE, (FIG. 2.)

Found in Ireland. Weight, 4 oz.; length, 8 inches; breadth at the hilt, $1\frac{3}{4}$ inches; breadth where broken, 1 inch.

1°. 21·40 grs. gave 22·98 grs. of oxide of copper = 85·70 per cent of copper.
2·73 grs. of oxide of tin = 10·02 per cent of tin.
·91 grs. of sulphate of lead = 2·89 per cent of lead.
·13 grs. of peroxide of iron = ·42 per cent of iron.

2°. 22·08 grs. gave 23·67 grs. of oxide of copper = 85·55 per cent of copper.
2·82 grs. of oxide of tin = 10·03 per cent of tin.
·96 grs. of sulphate of lead = 2·96 per cent of lead.
·15 grs. of peroxide of iron = ·47 per cent of iron.

	I.	II.
Copper . .	85·70	85·55
Tin . . .	10·02	10·03
Lead . . .	2·89	2·96
Iron . . .	·42	·47
	99·03	99·01

FRAGMENT OF A SWORD-BLADE, (FIG. 3.)

Found in Ireland. Weight, 6 oz.; length, 8½ inches; width at the broadest part, 1¾ inches; at the narrowest, 1¼ inches.

1°. 27·20 grs. gave 31·15 grs. of oxide of copper = 91·39 per cent of copper.
2·90 grs. of oxide of tin = 8·38 per cent of tin.

2°. 25·62 grs. gave 29·60 grs. of oxide of copper = 92·19 per cent of copper.
2·60 grs. of oxide of tin = 7·96 per cent of tin.

	I.	II.
Copper . .	91·39	92·19
Tin . . .	8·38	7·96
Iron and sulphur .	traces	traces
	99·77	100·15

BROKEN SPEAR-HEAD, (FIG. 4.)

Found in Ireland. Weight, 11½ oz.

1°. 29·05 grs. gave ·60 grs. of sulphate of baryta = ·28 per cent of sulphur.

2°. 29·40 grs. gave ·65 grs. of sulphate of baryta = ·29 per cent of sulphur.

	I.	II.
Copper . .	99·72	99·71
Sulphur . .	·28	·29
	100·00	100·00

CELT, (FIG. 5.)

Found in Ireland. Weight, about 10 oz.

1°. 26·0 grs. gave 29·40 grs. of oxide of copper = 90·23 per cent of copper.
2·49 grs. of oxide of tin = 7·50 per cent of tin.
·50 grs. of sulphate of lead = 1·31 per cent of lead.

2°. 27·0 grs. gave 30·84 grs of oxide of copper = 91·14 per cent of copper.
2·55 grs. of oxide of tin = 7·37 per cent of tin.
·50 grs. of sulphate of lead = 1·26 per cent of lead.

	I.	II.
Copper	90·23	91·14
Tin	7·50	7·37
Lead	1·31	1·26
Iron, cobalt, nickel and sulphur	traces	traces
	99·04	99·77

CELT, (FIG. 6.)

Weight, about 1 lb.

1°. 14·87 grs. gave 1·86 grs. of oxide of tin = 9·82 per cent of tin.

2°. 13·93 grs. gave 1·74 grs. of oxide of tin = 9·81 per cent of tin.

	I.	II.
Copper . .	90·18	90·19
Tin . . .	9·82	9·81
Iron . . .	trace	trace
	100·00	100·00

CELT, (FIG. 7.)

Weight, 4 oz.

1°. 30·80 grs. gave 34·50 grs. of oxide of copper = 89·38 per cent of copper.
3·60 grs. of oxide of tin = 9·18 per cent of tin.
·15 grs. of oxide of iron = ·34 per cent of iron.
26·40 grs. gave ·47 grs. of sulphate of baryta = ·24 per cent of sulphur.

2⁰. 25·00 grs. gave 27·97 grs. of oxide of copper = 89·28 per cent of copper.
2·93 grs. of oxide of tin = 9·21 per cent of tin.
·12 grs. of oxide of iron = ·33 per cent of iron.
13·99 grs. gave ·24 grs. of sulphate of baryta.

	I.	II.
Copper	89·38	89·28
Tin	9·18	9·21
Iron	·34	·33
Sulphur	·24	·24
	99·14	99·06

CELT, (FIG. 8.)

Weight, about 5¾ oz. Specific gravity = 8·09.

1⁰. 11·43 grs. gave 11·96 grs. of oxide of copper = 83·53 per cent of copper.
1·56 grs. of oxide of tin = 10·95 per cent of tin.
·54 grs. of sulphate of lead = 3·22 per cent of lead.
·10 grs. of peroxide of iron = ·61 per cent of iron.
·06 grs. of oxides of nickel and cobalt = ·41 per cent of metal.

2⁰. 11·36 grs. gave 11·92 grs. of oxide of copper = 83·76 per cent of copper.
1·57 grs. of oxide of tin = 11·09 per cent of tin.
·53 grs. of sulphate of lead = 3·18 per cent of lead.
·09 grs. of peroxide of iron = ·55 per cent of iron.
·04 grs. of oxides of nickel and cobalt = ·27 per cent of metal.

	I.	II.
Copper	83·53	83·76
Tin	10·95	11·09
Lead	3·22	3·18
Iron	·61	·55
Nickel and cobalt	·41	·27
	98·72	98·85

C.

COINS STRUCK SINCE THE COMMENCEMENT OF THE CHRISTIAN ERA.

LARGE BRASS OF NERO. A.D. 60.

Reverse: Rome seated.

Weight 435 grs. Specific gravity = 8·59. Metal of a bright yellow colour.

	I.	II.
Copper . . .	81·07	— *
Tin . . .	1·06	1·04
Zinc . . .	17·73	17·90
	99·86	

TITUS. A.D. 79.

Weight 178 grains. Specific gravity = 8·5 Metal yellow and soft.

1°. 20·41 grs. gave 21·30 grs. of oxide of copper = 83·27 per cent of copper.
4·06 grs. of oxide of zinc = 15·93 per cent of zinc.
·15 grs. of peroxide of iron = ·51 per cent of iron.

2°. 20·68 grs. gave 21·46 grs. of oxide of copper = 82·81 per cent of copper.
4·07 grs. of oxide of zinc = 15·76 per cent of zinc.
·15 grs. of peroxide of iron = ·50 per cent of iron.

	I.	II.
Copper . . .	83·27	82·81
Zinc . . .	15·93	15·76
Iron . . .	·51	·50
	99·71	99·07

HADRIAN. A.D. 120.

Fortunæ reduci.

Weight = 365 grains. Specific gravity = 8·30. This coin is finely patinated, and the metal of a fine yellow colour.

* Copper lost. This analysis was made for me by Mr. H. How.

1°. 15·07 grs. gave 16·20 grs. of oxide of copper = 85·78 per cent of copper.
·23 grs. of oxide of tin = 1·19 per cent of tin.
·40 grs. of sulphate of lead = 1·81 per cent of lead.
2·04 grs. of oxide of zinc = 10·81 per cent of zinc.
·16 grs. of peroxide of iron = ·74 per cent of iron.

2°. 12·17 grs. gave 13·05 grs. of oxide of copper = 85·57 per cent of copper.
·17 grs. of oxide of tin = 1·09 per cent of tin.
·295 grs. of sulphate of lead = 1·65 per cent of lead.
1·65 grs. of oxide of zinc = 10·86 per cent of zinc.
·13 grs. of peroxide of iron = ·74 per cent of iron.

	I.	II.
Copper . . .	85·78	85·57
Tin . . .	1·19	1·09
Lead . . .	1·81	1·65
Zinc . . .	10·81	10·86
Iron . . .	·74	·74
	100·33	99·91

FAUSTINA, JUN. A.D. 165.

Pietas.

Weight = 362 grains. Specific gravity = 8·83.

Coin without patina. Metal of a whitish colour and very brittle.

1°. 17·55 grs. gave 17·40 grs. of oxide of copper = 79·11 per cent of copper.
1·14 grs. of oxide of tin = 5·10 per cent of tin.
2·35 grs. of sulphate of lead = 9·13 per cent of lead.
1·41 grs. of oxide of zinc = 6·43 per cent of zinc.
·06 grs. of peroxide of iron = ·24 per cent of iron.

2°. 15·73 grs. gave 15·61 grs. of oxide of copper = 79·19 per cent of copper.
·97 grs. of oxide of tin = 4·84 per cent of tin.
2·13 grs. of sulphate of lead = 9·23 per cent of lead.
1·20 grs. of oxide of zinc = 6·11 per cent of zinc.
·05 grs. of peroxide of iron = ·22 per cent of iron.

	I.	II.
Copper . . .	79·11	79·19
Tin . . .	5·10	4·84
Lead . . .	9·13	9·23
Zinc . . .	6·43	6·11
Iron . . .	·24	·23
	100·01	99·59

GREEK IMPERIAL SAMOSATA. About A.D. 212.

Reverse: The city seated.

Weight=274 grains. Specific gravity=8·53. Metal of a greyish colour; very coarse and brittle. No patina.

1°. 23·85 grs. gave 21·12 grs. of oxide of copper=70·66 per cent of copper.
2·06 grs. of oxide of tin=6·78 per cent of tin.
7·70 grs. of sulphate of lead=22·01 per cent of lead.

2°. 17·74 grs. gave 15·82 grs. of oxide of copper=71·16 per cent of copper.
1·52 grs. of oxide of tin=6·73 per cent of tin.
5·70 grs. of sulphate of lead=21·91 per cent of lead.

	I.	II.
Copper . . .	70·66	71·16
Tin . . .	6·78	6·73
Lead . . .	22·01	21·91
Iron . .	faint trace	faint trace
	99·45	99·80

SMALL BRASS OF THE TIME OF THE THIRTY TYRANTS.

About A.D. 260.

VICTORINUS, SEN. (No. 1.)

Providentia Aug.

Weight=37·7 grains. Specific gravity=8·77. Metal rather hard, and not patinated.

14·96 grs. gave 17·88 grs. of oxide of copper = 95·37 per cent of copper.
0·19 grs. of oxide of tin=·99 per cent of tin.

Copper	95·37
Tin	·99
Lead	trace
Silver	1·60
Iron	trace
	97·96

VICTORINUS, SEN. (No. 2.)

Salus Aug.

Weight=37·6 grains. Specific gravity=8·73. Coin not patinated.

15·83 grs. gave 0·02 grs. of oxide of tin=·10 per cent of tin.
·23 grs. of peroxide of iron=1·00 per cent of iron.

Copper	97·13*
Tin	·10
Lead	trace
Silver	1·76
Iron	1·01
	100·00

TETRIUS, SEN. A.D. 267. (No. 1.)

Weight=37·3 grains.

21·07 grs. gave 26·01 grs. of oxide of copper = 98·50 per cent of copper.
·10 grs. of oxide of tin=·37 per cent of tin.
·14 grs. of peroxide of iron=·46 per cent of iron.

Copper	98·50
Tin	·37
Lead	trace
Silver	·76
Iron	·46
	100·09

* Copper lost, estimated by difference.

TETRIUS, SEN. A.D. 268. (No. 2.)

Weight = 45·25 grains.

26·15 grs. gave 32·15 grs. of oxide of copper = 98·00 per cent of copper.
·17 grs. of oxide of tin = ·50 per cent of tin.
·02 grs. of peroxide of iron = ·05 per cent of iron.

Copper	98·00
Tin	·50
Silver	1·15
Iron	·05
	99·70

CLAUDIUS GOTHICUS. A.D. 268. (No. 1.)

Spes publica.

Weight = 52·2 grains. Specific gavity = 8·81. Coin thinly covered with red patina. Metal rather hard.

18·23 grs. gave 18·65 grs. of oxide of copper = 81·60 per cent of copper.
1·72 grs. of oxide of tin = 7·41 per cent of tin.
2·17 grs. of sulphate of lead = 8·11 per cent of lead.

Copper	81·60
Tin	7·41
Lead	8·11
Silver	1·86
	98·98

CLAUDIUS GOTHICUS. A.D. 268. (No. 2.)

Juno Regina.

Weight = 58·3 grains. Specific gravity = 8·71.

22·44 grs. gave 23·82 grs. of oxide of copper = 84·70 per cent of copper.
·86 grs. of oxide of tin = 3·01 per cent of tin.
·88 grs. of sulphate of lead = 2·67 per cent of lead.
·10 grs. of peroxide of iron = ·31 per cent of iron.

Copper	84·70
Tin	3·01
Lead	2·67
Silver	7·93
Zinc	trace
Iron	·31
	98·62

TACITUS. A.D. 275. (No. 1.)

Libertas Aug.

Weight = 62·3 grains. Specific gravity = 8·72.

18·17 grs. gave 19·60 grs. of oxide of copper = 86·08 per cent of copper.
·84 grs. of oxide of tin = 3·63 per cent of tin.
1·30 grs. of sulphate of lead = 4·87 per cent of lead.

Copper	86·08
Tin	3·63
Lead	4·87
Silver	4·40
	98·98

TACITUS. (No. 2.)

Pax publica.

Weight = 49·5 grains. Specific gravity = 8·70.

13·61 grs. gave 15·60 grs. of oxide of copper = 91·46 per cent of copper.
·45 grs. of peroxide of iron = 2·31 per cent of iron.

Copper	91·46
Silver	5·92
Iron	2·31
	99·69

PROBUS. (No. 1.)

Succeeded Tacitus, who reigned only six months.

Clementia Temp.

Weight of coin, 52·2 grains. Specific gravity = 8·72.

16·06 grs. gave 18·25 grs. of oxide of copper = 90·68 per cent of copper.
·41 grs. of oxide of tin = 2·00 per cent of tin.
·55 grs. of sulphate of lead = 2·33 per cent of lead.
·28 grs. of oxide of zinc = 1·39 per cent of zinc.
·14 grs. of peroxide of iron = ·61 per cent of iron.

Copper	90·68
Tin	2·00
Lead	2·33
Silver	2·24
Zinc	1·39
Iron	·61
	99·25

PROBUS. (No. 2.)

Mars Victor.

Weight = 49 grains. Specific gravity = 8·74.

12·14 grs. gave 14·40 grs. of oxide of copper = 94·65 per cent of copper.
·07 grs. of oxide of tin = ·45 per cent of tin.
·08 grs. of sulphate of lead = ·44 per cent of lead.
·14 grs. of peroxide of iron = ·80 per cent of iron.

Copper	94·65
Tin	·45
Lead	·44
Silver	3·22
Iron	·80
	99·56

In addition to the foregoing analyses, the following estimations of silver were made by direct cupellation :

	Legend.	Weight of coin.	Percentage amount of silver.
		grs.	
Aurelian	Restituti orbis . . .	57·20	2·90
„	Fortuna redux . . .	50·50	2·96
Severina	Providentia Deorum . .	54·5	4·37
„	Concordia militum . .	54·0	5·80
Tacitus	Libertas Aug: . . .	61·4	4·90
Victorinus Sen. . .	Pax Aug:	38·0	2·20
„ „ . .	Providentia Aug : . .	35·7	1·10
Tetrius, Jun. . .	Pietas Aug:	31·5	·38
„ „ . .	„ „	44·0	·41
Quintillus . . .	Fides militum	52·4	2·32
„ . . .	„ „	33·8	2·25
Marius	„ „	43·7	5·15

TABLE, SHOWING THE MEAN COMPOSITIONS OF THE SPECIMENS ANALYSED.

	Date.		Copper.	Tin.	Lead.	Iron.	Zinc.	Silver.	Sulphur.	Nickel.	Cobalt.
	B.C.	A.D.									
ÆS	500	—	69·69	7·16	21·82	·47	—	—	trace	trace	·57
Semis	500	—	62·04	7·66	29·32	·18	—	—	trace	·19	·23
Quadrans	500	—	72·22	7·17	19·56	·40	—	—	trace	·20	·28
Hiero I.	470	—	94·15	5·49	—	·32	—	—	—	—	—
Alexander the Great	335	—	86·77	12·99	—	—	—	—	·06	—	—
Philippus III.	323	—	90·27	9·43	—	—	—	—	—	—	—
Philippus V.	200	—	85·15	11·12	2·85	·42	—	—	trace	—	—
Copper coin of Athens	?	—	88·34	9·95	·63	·26	—	—	—	trace	trace
Egyptian, Ptolemy IX.	70	—	84·21	15·64	—	trace	—	—	trace	—	trace
Pompey, First Brass	53	—	74·17	8·47	16·15	·29	—	—	—	—	—
Coin of the Atilia Family	45	—	68·69	4·86	25·43	·11	—	—	—	trace	trace
Julius and Augustus	42	—	79·13	8·00	12·81	trace	—	—	trace	—	—
Augustus and Agrippa	30	—	78·45	12·96	8·62	trace	—	—	trace	—	—
Large Brass of the Cassia Family	20	—	82·26	—	—	·35	17·31	—	trace	—	—
Sword-blade (Fig. 1.)	—	—	89·69	9·58	—	·33	—	—	trace	—	—
Broken sword-blade (Fig. 2.)	—	—	85·62	10·02	—	·44	—	—	—	—	—
Fragment of a sword-blade (Fig. 3.)	—	—	91·79	8·17	—	trace	—	—	trace	—	—
Broken spear-head (Fig. 4.)	—	—	99·71	—	—	—	—	—	·28	—	—
Celt, (Fig. 5.)	—	—	90·68	7·43	1·28	trace	—	—	trace	—	—
Celt, (Fig. 6.)	—	—	90·18	9·81	—	trace	—	—	—	—	—
Celt, (Fig. 7.)	—	—	89·33	9·19	—	·33	—	—	·24	—	—
Celt, (Fig. 8.)	—	—	83·61	10·79	3·20	·58	—	—	—	trace	·34
Large Brass of Nero	—	60	81·07	1·05	—	—	17·81	—	—	—	—
Titus	—	79	83·04	—	—	·50	15·84	—	—	—	—
Hadrian	—	120	85·67	1·14	1·73	·74	10·85	—	—	—	—
Faustina, Jun.	—	165	79·14	4·97	9·18	·23	6·27	—	—	—	—
Greek Imperial Samosata	—	212	70·91	6·75	21·96	trace	—	—	—	—	—
Victorinus, Sen. (No. 1.)	—	262	95·37	·99	trace	trace	—	1·60	—	—	—
Victorinus, Sen. (No. 2.)	—	262	97·13	·10	trace	1·01	—	1·76	—	—	—
Tetrius, Sen. (No. 1.)	—	267	98·50	·37	trace	·46	—	·76	—	—	—
Tetrius, Sen. (No. 2.)	—	268	98·00	·51	—	·05	—	1·15	—	—	—
Claudius Gothicus, (No. 1.)	—	268	81·60	7·41	8·11	—	—	1·86	—	—	—
Claudius Gothicus, (No. 2.)	—	268	84·70	3·01	2·67	·31	trace	7·93	—	—	—
Tacitus, (No. 1.)	—	275	86·08	3·63	4·87	—	—	4·42	—	—	—
Tacitus, (No. 2.)	—	275	91·46	—	—	2·31	—	5·92	—	—	—
Probus, (No. 1.)	—	275	90·68	2·00	2·33	·61	1·39	2·24	—	—	—
Probus, (No. 2.)	—	275	94·65	·45	·44	·80	—	3·22	—	—	—

D.

DEDUCTIONS.

We learn from the foregoing analyses that the metals entering into the composition of the brass of the earliest ages were copper, tin and lead, although the latter seldom occurs in any considerable quantity, except in the oldest specimens, and in many even of these, particularly in the early Macedonian coins, it is entirely wanting. The iron, cobalt and nickel, together with traces of sulphur, which sometimes occur, are evidently too small in quantity to have been intentionally added to the mixture, and consequently their presence must be rather ascribed to the localities from which the ancients drew their supply of ores, and the imperfect methods employed for their reduction, than to any design on the part of the artists. The cutting instruments which have been examined, are uniformly composed of copper and tin, with the occasional admixture of a small quantity of lead, which was probably added for the purpose of communicating a certain degree of toughness to the alloy, and it is also remarkable that the proportion of tin to that of copper, both in the celts and sword-blades, is very nearly as one to ten.

Zinc first makes its appearance a short time previous to the Christian era, and is continued in all the subsequent coins, although occasionally associated with lead and tin, until it almost entirely disappears in the small brass of the period of the Thirty Tyrants, when its place is supplied by a quantity of silver, varying from 0·76 to nearly 8 per cent, and which may perhaps have been intentionally added for the purpose of increasing the value of the metal.

In speaking of these coins, Pinkerton remarks: "It may be proper to observe, before leaving this part of my subject, that the metal used in the Parts of the Assarion, or in the small brass coins, is, as may be supposed, very little attended to by the ancients. In those of the first emperors, yellow brass is sometimes employed, but it is always of a refuse, or bad kind; as in the Semis of Nero, for instance, GENIO AVGVSTI. But copper is the general metal used in parts of the As, from the earliest times down to the latest; and if

sometimes brass be employed, it is never such as appears in the Sestertii and Dupondiarii, which is very fine and beautiful; but only the refuse. Yellow brass of the right sort seems to have totally ceased in the Roman coinage, with the Sestertius, under Gallienus; though a few small coins of very bad metal, of that hue, appear so late as Julian II."*

On referring to the table of analyses, we shall, however, perceive, that although the results obtained seem to confirm the assertions made relative to yellow brass, in the above quotation, yet that in no one instance, has a coin been found to consist of copper alone; and the only case in which this metal proved to be unalloyed, was in the spear-head, Fig. 4, found in Ireland. The largest proportion of lead occurs in the ancient Roman As, and its parts, in which it was probably employed for the purpose of rendering the alloy of which they consist easily fusible; for these coins being originally cast and not stamped like other money, a metal melting at a low temperature, would materially facilitate this operation.

The later coins, containing a large proportion of tin, seem to have been struck whilst the metal was still warm, as it would be impossible to obtain such sharp impressions as they usually bear, by the force of any blow applied on a metal so very hard and brittle, at ordinary temperatures.

Pinkerton states, that in the Roman mint, the alloy was first cast into the form of bullets, and that these were afterwards flattened and struck by the die, until an impression of sufficient depth was obtained. The appearance of many both of the Greek and Roman coins, indicates that the form of the blank pieces was spherical, but the metal of these very coins, is frequently so brittle, that they may easily be broken by a blow from the hammer, and could not have received their present form without being previously heated and struck whilst the metal was in a pasty state. That this was the method actually employed, is rendered very probable from some of the devices on the coins themselves, particularly on a Denarius of the Carisia family, bearing on the obverse, the head of Moneta, with name; and on the reverse, the implements used by the Romans in their coinage, viz., two dies, with the hammer and pincers; which is doubtless a correct representation of the apparatus employed in the Roman mint.† From the presence of the pincers in this design, it is almost certain that the metal was struck hot, as the blank could

* Vol. I, 126.

† Till on Coins, 7.

otherwise be more conveniently placed on the die by the hand, than through the intervention of tongs, which would rather embarrass than facilitate the operation.

With respect to the furnaces employed by the ancients, little information can be obtained, as these arts were formerly either held as secrets by a few individuals, who made a mystery of their operations, or they were too much despised by ancient authors, to afford them a subject for their writings; and we are consequently more indebted for our scanty knowledge of ancient metallurgy to the vestiges of primitive foundries, which have occasionally been brought to light in various parts of the world, than to any accounts which may have been transmitted to us from those remote times.

The first method of smelting ores, doubtless consisted in placing the mineral in heaps, together with several successive layers of wood, which being kindled, first roasted, and then reduced a portion of the material with which it was mixed. In Macedonia, where lead mines were worked in the time of Philip, the father of Alexander, large heaps of slag are found so far above the level of the rivers of the country, that the furnaces in which they were produced must have been worked either by bellows moved by human labour, or by the force of the prevailing winds alone.* We are also told, that the Peruvians were in the habit of melting their ores by the simple application of fire, or when they were of a very refractory nature, by means of furnaces so constructed on high ground as to yield a draught without the aid of bellows, a machine with which they were totally unacquainted.†

The boles of Derbyshire, many of which from the pigs of Roman lead found in their vicinity, may be presumed to be of great antiquity, were worked in a nearly similar manner, and continued to be thus carried on during several centuries, as this method of smelting was, according to Childrey, not quite extinct in the seventeenth century, who, in speaking of the Peak, says: "The lead-stones in the Peak, lie but just within the ground, next to the upper crust of the earth. They melt the lead on the top of the hills that lie open to the west wind; making their fires to melt it as soon as the west wind begins to blow, which wind, by long experience, they find to hold longest of all others. But for what reason I know not, since I should think lead

* Watson's Chemical Essays, III, 265.

† Alonso Barhu.—Treatise on Metals, French translation, I, 272.

were the easiest of all metals to melt, they make their fires extraordinary great."*

Discoveries made by various travellers in Russia, during the last century, throw considerable light on the subject of mining and metallurgy as anciently practised in that part of the world. The remains of numerous mines have been traced by Gmelin, Lepechin and Pallas, on the southern and eastern borders of the Ural Mountains; and in them were found hammers and chisels of copper, as well as various instruments of the same metal, of which the uses are at present unknown. From the absence of any remains of masonry in the neighbourhood, these excavations are inferred to have been made by a nomadic people, probably the Scythians; and from no iron tools having been found in any of them, we may conclude that these operations were carried on before the conquest of Siberia by the Tartars, who effected the subjugation of that part of Asia, about 150 years before our era.† Sledges made of large stones, to which handles had been attached, were also discovered, together with boars' fangs, with which the gold appears to have been collected, and leathern bags or pockets in which it was preserved. With such imperfect tools, the progress made must necessarily have been exceedingly slow, and in one instance, after reaching a band of rock and penetrating it for a short distance, the miners seem to have lost patience and abandoned the works. The pits or shafts are well made, about seven feet in diameter, and of a circular form, some of them being twenty fathoms in depth. The passages and props are also well executed, but the former so low and narrow, that they could only have been excavated with the greatest difficulty to the workmen. The ores when extracted, were carried to the nearest rivulet for the purpose of being crushed and washed, which operations were probably dispensed with in the richest varieties, which were sometimes melted in the mines themselves, metallic copper, together with slag, and the tools employed in melting and refining, having been found in some of them.

Lumps of copper, which contain no traces of gold, have also been discovered, although the copper ores of the districts are found associated with that metal, and it is therefore evident that the ancient people who worked these mines were acquainted with a method of refining gold.

* Childrey's Britain, 1661.

† Histoire Généalogique des Tartares.

The smelting was effected in small furnaces made of red bricks, and of which Gmelin found nearly a thousand in the eastern parts of Siberia. The height and breadth of these were about two feet, and the width three. They were also furnished with holes in two of their opposite sides, the one for the introduction of bellows, and the other for the escape of the metal and slags. In the neighbourhood of the furnaces were found large quantities of broken pottery, together with numerous heaps of scoriæ, which indicate that operations to a very considerable extent, have at some period been carried on in that locality.

Gmelin likewise found in the same districts the remains of various furnaces which had been employed for the extraction of silver, and remarked that the lead with which it was associated had been thrown away in the scoriæ, whilst the whole of the silver was carefully extracted. By what means this was effected, in this particular case, is of course impossible for us to say, although it is highly probable that cupellation in some form was resorted to. Diodorus, [III, 14,] informs us, that gold was purified, by being melted and heated in earthen pots, together with an alloy of tin and lead, to which salt and barley-bran were added, and that the fire was kept up during five successive days. Another ancient author* states, that gold was melted by a gentle fire with the addition of salt, nitre and alum, and that the same process was employed for refining silver. It is, however, difficult to understand what action these substances, with the exception of the nitre, could have on the purification of silver and gold, and we may therefore conclude, that the action of the air was after all the chief means of oxidation employed.†

In Britain, silver mines were worked before the invasion of the island by the Romans, and gold must also have been well-known to the inhabitants before the arrival of Cæsar, since coins of that metal were then in circulation. Cæsar and Strabo both state that the Britons obtained their copper from foreign countries, and we may hence infer that the art of refining this metal was either unknown, or little cultivated by our forefathers at that remote period. Iron is described by Cæsar as being so rare, that pieces of it were sometimes used as a medium of exchange, and almost as highly valued as gold; but a century afterwards it had become very common, as in Strabo's

* Hippocrates de Diæta, 193.

† The nitre of the ancients was probably carbonate of soda.

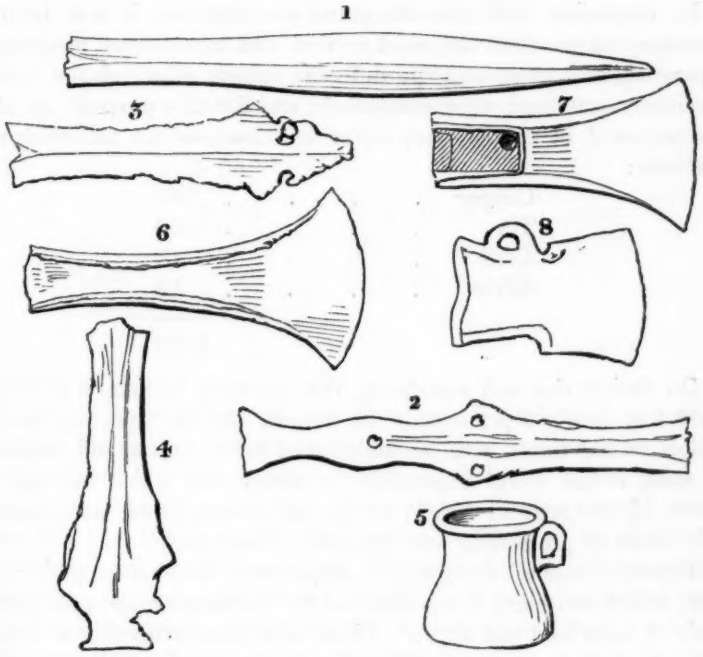
time, it was an article of exportation.* Tin was anciently the most celebrated product of Britain, and appears even at that time to have been extracted in considerable abundance, since it was the desire of obtaining possession of these mines, and becoming thereby independent of the Phœnician monopoly, which first induced the Romans to visit the island. Before the conquest of their country, the Ancient Britons extracted this metal from its ores by methods which they had themselves discovered, and which were probably improved on by their conquerors.† The smelting process would seem to have been very simply conducted. The broken ore was placed in a hole in the ground, the sides of which were lined with pieces of wood, which, on being ignited, reduced the lead and tin, which were separated from the slags by being run off through a narrow channel into another receptacle. Many of these rude furnaces have been found in various parts of Cornwall and elsewhere, in which not only charcoal and slags have been discovered, but also portions of the reduced metal, which in many instances, had, from long exposure to oxidising influences, again become partially converted into tin ore.‡ This very rude method must have been attended with considerable success, as the slags resulting from it have proved on examination to contain but a small amount of metal.§

From these and many other relics which have been met with in different parts of the world, we may infer, that although the arts of working the metals were carried on formerly on a much smaller scale than at the present day, the operations of the early metallurgists were tolerably successful, and that in spite of the rude apparatus which they employed, the results obtained by them were generally of a satisfactory nature.

That a great degree of attention was at a very early period bestowed on the manufacture of alloys destined for particular purposes, is proved by the uniform composition of the several cutting instruments examined; although it is evident that but little care was taken to obtain a correct standard for the early brass money, as many pieces of nearly the same date, and of similar value, differ materially in the amounts of the metals of which they consist. On this subject I shall offer no observations, as the object of the present paper is rather to show the composition and proportions of the ancient alloys, than to enter into a discussion on the coins of antiquity, and I therefore leave

* Strabo, IV, 305.
† Strabo, I.
‡ Jews' house tin.
§ Pennant, I, 58.

this matter for the consideration of the numismatist and antiquarian, whose labours in that direction may possibly be, in some measure, aided by the facts elicited from the foregoing analyses.



No. 1. Sword-blade, found under Chertsey Bridge, Thames.
„ 2. A broken sword-blade, from Ireland.
„ 3. „ „ also found in Ireland.
„ 4. A broken spear-head, from Ireland, presenting the only specimen of unalloyed copper examined.
„ 5. A celt, with a socket for the introduction of a wooden handle and an eye, probably for the purpose of attaching a string.
Nos. 6 and 7. Celts, composed of a harder alloy, and without sockets.
No. 8. A celt, with socket and loop, found in Ireland, and made of a hard alloy. This specimen appears to have been sharpened by grinding.

E.

APPENDIX.

In connexion with the foregoing investigation, it was thought necessary to ascertain the most correct and expeditious methods of separating and estimating the different metals of which the various specimens examined were composed; and for this purpose, an alloy was prepared of copper, tin, silver and lead, in the following proportions:

Copper	880
Tin	100
Lead	10
Silver	10
	1000

On fusing this and examining the resulting button, it proved to have lost nearly 2 per cent of its weight, and by repeating the operation several times, with the addition of borax, tartar and carbonate of soda, it was found impossible to obtain one which had not lost above 1½ per cent in weight of the metals employed, and therefore this mode of proceeding was ultimately abandoned.

Twenty grains of electrotyped copper were next taken, and to this were added two parts of tin obtained by the same means, and a grain each of pure lead and silver. These were placed together in a flask, and attacked by strong nitric acid; the excess of which was subsequently evaporated off. Water was then added, and the oxide of tin thrown on a filter and washed. The silver was afterwards precipitated as chloride, by hydrochloric acid, so diluted as not to cause a turbidity in solutions of salts of lead—washed by decantation—and collected, fused and weighed, in a small porcelain capsule.

From the liquor decanted from the chloride of silver, the lead was precipitated by means of an excess of dilute sulphuric acid. The whole was then evaporated to dryness, the residue treated with water, and the sulphate of lead washed first with water containing a little sulphuric acid, and afterwards with alcohol. The filtrate from the sulphate of lead was then evaporated nearly to dryness, in order to get rid of the alcohol and nitric acid; and to the solution of the copper-salts in water, ammonia was added in excess. The blue liquor was then poured into a well-ground stoppered bottle, which being filled with boiling distilled water, and a weighed piece of pure copper placed in

it was set aside according to the method of Levol, until it became colourless. Two experiments were made on the foregoing weights, and the following results obtained:

1°.	Tin .	2·027	=	Oxide of tin .	2·58
	Silver .	·948	=	Chloride of silver	1·26
	Lead .	·982	=	Sulphate of lead .	1·44
	Copper .	24·030			
		27·987			
2°.	Tin .	2·012	=	Oxide of tin .	2·56
	Silver .	·956	=	Chloride of silver	1·27
	Lead .	·995	=	Sulphate of lead .	1·46
	Copper .	23·620			
		27·583			

In the above analyses, it will be observed that there is a small excess on the tin, occasioned by the tendency of the peroxide of that metal to form stannates, and the consequent difficulty of obtaining the metastannic acid quite free from the oxides of the metals with which it was associated. A slight loss also occurs both on the silver and lead, occasioned in the former by the difficulty of collecting and estimating small quantities of the chloride, and in the latter case from sulphate of lead being slightly soluble in the copper filtrate.

The amount of copper given, is from fifteen to twenty per cent above the truth, as it was found impossible in practice to exclude the air from the bottles, and expel it from the solution with which they were filled, so perfectly as would be necessary, in order to obtain good results.

Several trials were afterwards made both by myself and an assistant, in order to test the correctness of this method, but in every case, a considerable excess was obtained.*

This way of estimating the copper, not having proved sufficiently accurate, I next tried the method of Pelouze. For this purpose, a solution of sulphuret of sodium was prepared; so diluted, that, in the first experiment, sixty divisions of the graduated burette with which it was measured, represented one grain of pure copper; in the second, 60¾ divisions were required to precipitate this amount of metal; and

* Mr. Hutchison, in his experiments, always got an excess of at least 2 per cent.

in the third operation, a quantity corresponding to nearly 62 graduations to the grain was employed before the whole of the copper was thrown down. These determinations were continued until, at the tenth experiment, rather more than 65 divisions were required to precipitate from the ammoniacal solution of copper one grain of metal. The absorption of oxygen from the air, and the consequent conversion of a portion of the sulphuret into hyposulphite of soda, having been found to proceed with such rapidity, this method of estimation was also abandoned; and on examining, on the following day, the air contained in the half-emptied bottle of solution, the oxygen had become completely absorbed.

The next experiment was made on a mixture of copper, tin, lead and silver, in the same proportions as in the foregoing analyses; and the operations were conducted in a precisely similar manner as far as regards the tin and lead, except that the latter was in this instance thrown down as sulphate, before the precipitation of the silver by hydrochloric acid, and that dilute sulphuric acid only was used for washing. The precipitated chloride, instead of being washed by decantation and afterwards fused and weighed, was collected on a filter, dried, and the filter incinerated without carrying the heat so far as to melt the chloride and cause it to attach itself to the sides of the crucible. The filter-ash and chloride were then mixed with about five grains of carbonate of soda, and one of tartrate of potash, carefully enveloped in a hundred grains of pure lead-foil, placed in a crucible containing a mixture of borax and carbonate of soda, and fused into a button which was afterwards passed to the muffle. This method of treatment, although not possessing the advantages with regard to accuracy which are offered by direct cupellation, is nevertheless more easily conducted and freer from sources of error than weighing such a minute quantity of the chloride; and in cases where the small amount of materials to operate on excludes the possibility of a separate determination of that metal, as in the case of the small brass coins, I have found this modification succeed extremely well. The quantity of lead should, however, be large in proportion to the amount of chloride of silver, and if the lead-foil be in any degree argentiferous, the extent should be ascertained by a separate operation, and its weight deducted from the result.

The copper was precipitated by pure alcoholic potash in the state of oxide, which after being completely washed, was ignited and weighed in the usual way. This experiment gave the following results:

1°. Tin	2·027	=	Oxide of tin	2·58
Silver	·970			
Lead	·982	=	Sulphate of lead	1·44
Copper	20·009	=	Oxide of copper	25·10
	23·988			

2°. Tin	2·027	=	Oxide of tin	2·58
Lead	·975	=	Sulphate of lead	1·43
Silver	·975			
Copper	19·981	=	Oxide of copper	25·04
	23·958			

The above results being considered satisfactory, this method was adopted in the whole of the analyses.* Small quantities of iron, together with traces of cobalt and nickel, generally made it necessary to precipitate the copper first as sulphuret, which was afterwards re-dissolved and precipitated by caustic potash; the iron was then separated from cobalt and nickel by means of benzoate of ammonia, and the two latter, when not estimated together, were separated by cyanide of potassium. I have not, however, thought that such small quantities of these two metals can be separated with any great degree of accuracy, and have, therefore, been sometimes content to weigh them together.

* A paper was read January 28th, 1850, before the Royal Irish Academy, on "The Analysis of certain gold-coloured Bronze Antiquities," by Mr. Donovan, who employed a very different method to obtain his results. The author of the paper referred to, is of opinion that in the ordinary process of attacking such alloys, by means of nitric acid in a glass flask, a certain amount of loss is sustained, and that this is occasioned by a portion of the copper being carried off in combination with the gaseous oxides of nitrogen evolved. To obviate this inconvenience, and render his analyses more accurate, this gentleman made his attacks in a tubulated retort, to which he adapted a series of Woulfe's bottles, containing liquid ammonia, which on being evaporated to dryness, yielded a trace of oxide of copper, to be added to that obtained either in the usual way, by precipitation, or by the direct decomposition of the nitrate.

On repeating these experiments, I failed to obtain the smallest quantity of copper, even in the first Woulfe's bottle, when care was taken to use a large retort, and to prevent violent effervescence by the cautious addition of the acid. When this was not sufficiently attended to, or a retort of too small capacity was employed, faint traces of copper could be detected in the first bottle, but never in the second. It would therefore appear that the copper is then carried over mechanically by the gases given off, and the most simple means of preventing loss would be to employ a tolerably large flask for the attack, and to avoid, as much as possible, any very violent action on the alloy.

The presence of sulphur was detected, and its amount estimated, when lead was not present in the alloy, by the addition of chloride of barium to the filtrate from the metastannic acid, and the subsequent weighing of the sulphate of baryta formed. When lead was present, a trace of sulphuric acid was also sometimes found in the form of the sulphate of the oxide of that metal. This was of course precipitated, and, on filtration, remained with the oxide of tin on the filter. On digesting this, together with the trace of sulphate of lead, in a solution of carbonate of soda, carbonate of lead and sulphate of soda were obtained. On neutralizing the excess of carbonate of soda by nitric acid and evaporating to dryness, the filtrate from the residue taken up by water yielded, on the addition of chloride of barium, a faint turbidity; but in a very few instances only were the amounts of sulphate of baryta sufficient to allow of its being weighed.

On Chromic Acid and Sesquioxide of Manganese. By A. J. FAIRRIE, Esq.—When chromate of potash is added to a soluble salt of manganese, a chocolate-coloured precipitate subsides, which when dried at 212°, has, according to the analysis of Warington and Reinsch,* the formula $2\,MnO, CrO_3 + 2\,Aq$. Mr. Danson, however, in working on the chromates, ascertained that the precipitate produced as above, is not a true chromate of manganese, but a salt composed of chromic acid and sesquioxide of manganese, mixed with a definite quantity of sesquioxide of chromium; for, on dissolving the precipitate in dilute nitric acid and adding potash, the precipitated sesquioxide of manganese gave indications of the presence of sesquioxide of chromium; hence the excess of manganese in Warington's analysis, the manganese having been determined by precipitation with potash.†

With the view of reconciling the discrepancies between these statements, Mr. Fairrie prepared a large quantity of the compound, by mixing chloride of manganese with chromate of potash, collecting the precipitate on a filter, washing thoroughly, and drying at 212°. The chromic acid was determined by boiling the salt repeatedly with potash, filtering, neutralizing with acetic acid, and precipitating by acetate of lead. To determine the sesquioxide of manganese, the salt was fused with nitre and carbonate of potash, and the fused mass boiled with dilute alcohol to decompose the permanganate, &c. The water was determined in the usual way, and the sesquioxide of chromium by loss.

* Gmelin's Handbuch (Translation), IV, p. 248.
† Chem. Soc. Trans., 1842, p. 31.

The following were the results obtained:

		Calculated.	Found.	
$3\,Mn_2\,O_3$	240	45·71	45·12	45·84
$3\,Cr\,O_3$	153	29·14	28·40	
$Cr_2\,O_3$	78	14·85	15·66	
$6\,HO$	54	10·30	10·82	10·74
	525	100·00	100·00	

The salt appears to be formed by the action of 7 equivs. of chromate of potash on 6 equivs. of chloride of manganese.

On the Chromate of Alumina. By A. J. FAIRRIE, Esq.—When chromate of potash is added to a solution of alum, a bulky yellow, flocculent precipitate is formed, which is easily soluble in excess of the alum. This precipitate, when thoroughly washed, gave the following results on analysis:

		Calculated.	Found.
$Cr\,O_3$	51	30·72	32·36
$Al_2\,O_3$	52	31·32	31·25
$7\,HO$	63	37·96	36·39
$Al_2\,O_3, Cr\,O_3 + 7\,Aq.$	166	100·00	100·00

Chromic acid, therefore, has not a great affinity for alumina, as it readily forms with it a basic salt. The first washings of the precipitate appeared to contain an acid chromate of alumina.

Chromate of alumina is soluble in acetic acid and ammonia, but insoluble in chloride of ammonium.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

March 31, 1851. Anniversary Meeting.

The President, in the Chair.

The Report of the Council and the Audited Account of the Treasurer were read, and the Society proceeded to the election of Council and Officers for the ensuing year, when the following Gentlemen were declared to be duly elected: — President: Charles Daubeny, M.D., F.R.S.—Vice-Presidents: W. T. Brande, F.R.S., W. A. Miller, M.D., F.R.S., Robert Warington, Esq., Lyon Playfair, F.R.S.—Secretaries: B. C. Brodie, Esq., F.R.S., Theophilus Redwood, Esq. Foreign Secretary: A. W. Hofmann, Ph.D., F.R.S.—Treasurer: Robert Porrett, Esq., F.R.S.—Other Members of the Council: Thomas Andrews, M.D., F.R.S., John Blyth, M.D., William Ferguson, Esq., Edward Frankland, Ph.D., Warren De La Rue, F.R.S., H. Bence Jones, M.D., F.R.S., J. P. Joule, Esq., F.R.S., G. D. Longstaff, M.D., Thomas Graham, F.R.S., George Wilson, M.D., John Stenhouse, Ph.D., F.R.S., A. W. Williamson, Ph.D.

The thanks of the Society were voted to the President, Officers and Council for their services during the past year, and the Meeting was adjourned.

AUDITED REPORT OF THE TREASURER.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. *Cr.*

1850.		£.	s.	d.	1851.		£.	s.	d.
March 25.	To Balance from last Account	282	4	2	March 31.	By Purchase on 28th of May last of £150, 3 per cent. Consols, in name of Chemical Society, at 96¼, with Brokerage, 3*s.* 9*d.*	144	11	3
1851.									
March 31.	„ Subscriptions £349, and Compositions £70, since received	419	0	0	„ „	„ Brokerage on making transfer of £250, 3 p. c. Consols, from the name of R. Porrett, as Treasurer, to the name of the Chemical Society of London, incorporated by Royal Charter, 12th Victoria	0	3	1
„ „	„ Donations from sundry Members towards refunding the expenses of the Charter . .	3	8	6					
„ „	„ Ditto towards the Library Fund . . .	1	11	0					
„ „	„ Admission Fees from 17 new Members . .	34	0	0					
„ „	„ Proceeds from Sale of "Memoirs," &c. . .	3	4	4	„ „	„ Payment to H. Baillière, Publisher, for the "Journal," £118 1*s.* 0*d.*; and for Books, £10 2*s.* 6*d.*	128	3	6
					„ „	„ Ditto to R. and I. Taylor, for Printing, as per bill.	11	14	6
					„ „	„ Ditto to Ditto, for "Philosophical Magazine" .	1	15	0
					„ „	„ Ditto to Williams and Norgate, for Foreign Journals	6	18	0
					„ „	„ Ditto to D. Nutt, for Books	0	7	6
		£ 743	8	0	„ „	„ Ditto to H. Medlock, for Books . . .	4	2	6
					„ „	„ Ditto to J. Crandal, for Bookbinding . .	6	7	10
					„ „	„ Ditto to H. Watts, for One Year's Salary as Editor of the "Journal"	50	0	0
					„ „	„ Ditto to H. Medlock, for One Year's Salary to Christmas, 1850	25	0	0
					„ „	„ Ditto to Ditto for Petty Cash	5	3	8
					„ „	„ Ditto to F. H. Abel, for Translations . .	2	0	0
					„ „	„ Ditto to John Chapman, for One Year's Rent, to November, 1850	55	5	0
					„ „	„ Ditto to Ditto, for Tea, Coffee, &c. . . .	8	0	0
					„ „	„ Ditto to Servants at Mr. Chapman's . .	1	0	0
					„ „	„ Ditto to C. and E. Layton, for Seal Engraving .	0	16	0
					„ „	„ Ditto to Cavendish Society, Annual Subscription, 1850 to 1851	2	2	0
					„ „	„ Ditto to J. Churchill, for a Book-case . .	4	7	0
					„ „	„ Ditto to E. Pritchard and Sons, for Carpentry .	0	14	5
					„ „	„ Collector, for Poundage, including Stamps, &c.	18	8	6
					„ „	„ Postage, Stationery, Stamps, &c. . . .	2	9	3
					„ „	Balance carried to new Account	263	9	0
						London, March 31, 1851. £	743	8	0
						R. PORRETT, Treasurer.			

NOTICES

OF

PAPERS CONTAINED IN THE

"Philosophical Transactions" and Foreign Journals.

Researches on the Organic Bases.

By Dr. A. W. Hofmann, F.R.S.

From the "Philosophical Transactions," abstracted by the Author.

ACTION OF BROMIDE AND IODIDE OF ETHYL UPON TRIETHYLAMINE.

In a former paper, read before the Royal Society,* I have stated that a mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed up in a tube, solidified after several hours ebullition, and that the crystals consisted chiefly of the fibrous hydrobromate of triethylamine, with which however a certain quantity of white opaque granular crystals invariably was mixed. I have endeavoured to increase the quantity of the latter by using both the bromide of ethyl and the triethylamine in the anhydrous state. But by thus changing the conditions of the formation, the progress of the reaction is retarded in the most remarkable manner, days elapsing before the conversion is completed. While engaged in these experiments, I found that the result intended may be obtained almost instantaneously by substituting the iodide for the bromide of ethyl; and as this observation was immediately followed by a perfect elucidation of the whole question, I have scarcely returned again to the use of the bromide.

On adding perfectly anhydrous iodide of ethyl to triethylamine dried over hydrate of potassa, the mixture becomes slightly turbid, heat being evolved at the same time. At the common temperature the action goes on very gradually, and after the lapse of several days, the mixture is converted into a solid mass. On the other hand, if the mixture be exposed for a minute or two to the temperature of boiling water, a very powerful reaction ensues; the liquid remains, even after the removal of the source of heat, for some time in a state of lively ebullition, and solidifies after cooling, into a hard mass of

* Philosophical Transactions, Part I. 1850, p. 93.

crystals, which is snow-white or of a yellowish tint, according as either the triethylamine or the iodide of ethyl has been in excess. To avoid losing iodide of ethyl, and especially triethylamine, which is the result of a long series of troublesome and expensive processes, I have usually performed the reaction in strong glass tubes, of between three and four feet in length, which were sealed before the blowpipe after the substances had been introduced.

The crystalline mass produced in this reaction readily dissolves even in cold water. If the iodide was in excess this substance separates in heavy oily globules, which may be readily separated and recovered by distillation, and the solution is inodorous, and either neutral or very slightly acid; in the latter case it has always a marked yellowish tint. On the other hand, if the base was in excess, the solution of the crystals is colourless and alkaline; the alkaline reaction disappears however on ebullition, triethylamine being disengaged. The crystals are likewise soluble in alcohol, but almost insoluble in ether.

The purification of the crystals is not attended with any difficulties; it is in fact sufficient to dissolve them in cold water and to allow the solution to evaporate spontaneously, when beautiful well-defined white crystals of considerable size are deposited, which may be easily separated by mechanical means, from small quantities of a reddish iodine-compound, which is sometimes formed by the action of the air. This latter substance is formed in much larger quantity at higher temperatures, wherefore it is advisable to avoid the use of boiling water in the purification.

The crystals are anhydrous: when exposed to the temperature of boiling water they exhibit no change in weight. Their analysis led to the formula

$$C_{16}\,H_{20}\,N\,I.$$

Hence it would appear that the formation of the white crystals simply depends upon a direct combination of triethylamine with iodide of ethyl, for

$$\underbrace{C_{12}\,H_{15}\,N}_{\text{Triethylamine.}} + \underbrace{C_4\,H_5\,I}_{\text{Iodide of Ethyl.}} = \underbrace{C_{16}\,H_{20}\,N\,I.}_{\text{New crystalline compound.}}$$

In perfect accordance with this formation is the change which the iodine-compound undergoes when subjected to the action of heat; when rapidly heated the crystals fuse and are decomposed, the products being triethylamine and iodide of ethyl, which form two layers in the receiver, but rapidly unite again to the original compound. In fact this recombination takes place to a considerable extent in the neck of the retort; so that when first I became acquainted with this

substance, I was for some time under the impression that the iodine-compound might be volatilized without decomposition.

On adding potassa to a solution of the iodine-compound in water, the liquid solidified at once into a crystalline mass, which I took of course for the base existing in the iodide; analysis however soon showed that the substance thus precipitated is nothing but the iodide itself, which is less soluble in an alkaline solution than in pure water. The iodide was now distilled with a very concentrated solution of potassa for several hours; but during this time nothing but pure water passed over; the solution in the retort solidified on cooling to crystals of the unchanged iodide. When the solution of the iodide in potassa had become very concentrated, it separated into two layers, an aqueous one and an oily one, which floated on the surface. But even now no decomposition had been induced, the oily stratum solidifying on cooling into a crystalline cake of iodide perfectly unaltered. It was only when the liquid was evaporated to dryness that a change took place; but then the change was no longer due to the action of the potassa, but to the influence of heat, and in no way differed from the decomposition which the crystals undergo when heated alone.

However, the iodine, though it cannot be eliminated from the crystals by the alkalies, may be separated with the greatest facility by silver-salts; in fact, the nitrate, the sulphate, the oxide of silver, behave with the iodine-compound exactly as with iodide of potassium or sodium. On adding nitrate of silver to a solution of the iodide, iodide of silver is at once precipitated and a nitrate remains in solution, which on evaporation crystallizes in deliquescent needles. With sulphate of silver, a perfectly similar change takes place, an analogous sulphate remaining in solution. During these interchanges the liquid remains perfectly neutral. If the solution of the iodide be digested with freshly precipitated protoxide of silver, the solution at once assumes a powerfully alkaline reaction, iodide of silver being formed: the same effect is produced by the action of caustic baryta upon the sulphate, sulphate of baryta being precipitated. These reactions, when viewed collectively, exhibit a striking analogy between the new iodide and the metallic iodides, especially those of the alkali-metals. In fact the molecular group combined with iodine, in the compound under examination, behaves like sodium or potassium, it is a true organic metal in all its bearings. For this metal I propose, on the ground of its formation and composition, the name Tetrethyl-ammonium (*τέτρα*), which implies that it is built up by the intimate union of nitrogen with four equivalents of the hypothetical hydrocarbon called ethyl, and that it may be viewed as ammonium, in which the whole of the hydrogen is replaced by an equivalent proportion of the above hydrocarbon.

Ammonium. Tetrethylammonium.

$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}N. \qquad \left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N=C_{16}H_{20}N.$$

The new crystalline compound, according to this mode of viewing it, must be considered as iodide of tetrethylammonium, and its formation takes place in consequence of a transposition of the elements, which is perfectly analogous to that assumed by the followers of the ammonium-theory, in the formation of iodide of ammonium from ammonia and hydriodic acid.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+ \quad HI=\left\{\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}N\right\}I.$$

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N+C_4H_5I=\left\{\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}\dot{N}\right\}I.$$

Among the various substances derived from the new iodide, the corresponding oxide, the compound corresponding to oxide of ammonium attracted my attention in a pre-eminent degree.

Oxide of Tetrethylammonium.

I have already briefly stated how this substance is prepared; on decomposing the iodide with an excess of sulphate of silver, a sulphate is obtained, from which sulphuric acid and excess of silver may be separated by baryta. This was in fact the first process by which I separated the base; it is, however, difficult to obtain the solution in this manner free from either baryta or sulphuric acid; nor have I ever used this process again, after I had found that digestion with freshly precipitated protoxide of silver produces at once the same effect. The oxide is added in small proportions to the solution of the iodide, which is gently heated; it is immediately converted into yellow iodide of silver, which assumes a white colour on stirring, as long as any undecomposed iodide is in solution. Gradually the yellow colour becomes permanent, and the decomposition is complete as soon as an excess of unchanged oxide becomes perceptible by its colour.

On filtering off the silver-precipitate, a clear and colourless liquid is obtained, which contains the isolated base in solution. It is of a powerfully alkaline reaction, which manifests itself, not only in its deportment with vegetable colours, but also in its possessing the pungent bitterness of quinine; the solution, when strongly concentrated, not only burns the tongue, but it acts upon the epidermis,

which it destroys like caustic potassa or soda. On rubbing a solution of the oxide between the fingers, the well-known sensation produced by the fixed alkalies under the same circumstances is felt, and we perceive moreover the same peculiar odour.

Oxide of tetrethylammonium saponifies the fats as readily as potassa. The experiment was made with cocoa-nut oil, which after half an hour's ebullition with the new alkali was converted into a beautiful soft soap, having the appearance of an ordinary potassa-soap. This soap washes very well.

I have traced the analogy of the new body with potassa in many other directions. Chemists recollect the remarkable effect produced by ebullition with potassa in certain nitrogenous substances. It was by this process that Dr. Fownes, the discoverer of this reaction, converted furfuramide into the isomeric alkaloid, *furfurine*. I found that boiling with oxide of tetrethylammonium effects this molecular change as rapidly as potassa.

Like potassa it decomposes oxalic ether into oxalic acid and alcohol, and evolves ammonia from ammonia-salts, even in the cold. It may be substituted for potassa in Trommer's well-known sugar-test. Copper-solutions, mixed with either cane- or grape-sugar, yield on addition of oxide of tetrethylammonium, a light-blue precipitate of the hydrate of the protoxide, which redissolves in an excess of the base forming a deep blue solution, with a shade of green; on ebullition the cane-sugar solution deposits a greenish precipitate, which is only slowly and always very incompletely converted into suboxide of copper. In the presence of grape-sugar the reduction ensues instantaneously on application of heat.

The reactions of the new base with metallic oxides assimilate this compound as nearly as possible to the fixed caustic alkalies. In fact, the salts of the metals, with the exception of those of chromium, whose oxide does not redissolve in an excess of the base, exhibit the same reactions with potassa and oxide of tetrethylammonium.

Although I did not anticipate great results from the experiment, I have submitted the new base to the action of the galvanic current, the pile being disposed as in Berzelius's original experiment on the formation of the ammonium-amalgam. However, no phenomenon, other than the decomposition of water, was observed. This decomposition certainly appeared to be facilitated, especially if the base was employed in the form of sulphate. Nor had potassium-amalgam the slightest effect upon oxide of tetrethylammonium.

I must still mention a peculiar reaction, somewhat singular at the first glance, which takes place on adding the concentrated oxide to alkaline solutions of iodide of potassium, when the crystalline iodide of tetrethylammonium is at once precipitated. I need scarcely remark that this phenomenon is due to the insolubility of the iodide in alkaline solutions, and not to the new base possessing a greater

affinity for iodine than potassium, whose oxide is thus actually liberated.

A moderately concentrated solution of oxide of tetrethylammonium may be boiled without alteration; it is only in a very advanced stage of evaporation that decomposition gradually sets in. The change occurs even in the water-bath, as soon as the base becomes nearly dry. On evaporating, however, under the bell of the air-pump in the presence of sulphuric acid and lime, the base may be obtained in the dry state. I have endeavoured to obtain it in this manner in a condition fit for analysis, but all my attempts have been hitherto in vain; a concentrated solution of the oxide when placed in a vacuum, deposits after some days' exposure, long hair-like needles, which are, however, deliquescent in the extreme, and attract carbonic acid with great avidity. In both respects they are scarcely inferior to potassa. By remaining longer *in vacuo*, these crystals disappear again, and the whole liquid dries up to a semi-solid mass, which also deliquesces rapidly, and becomes carbonated on exposure to the air. As there was not the slightest chance of getting this substance into a combustion tube, I endeavoured to ascertain its composition, by decomposing a known quantity of the iodide with protoxide of silver, evaporating *in vacuo* in a glass dish, which on being removed from the air-pump, could be covered with a glass plate, and determining the weight of the solid mass remaining. These experiments, however, have not led to any decisive results. Soon after the formation of the crystals, the liquid becomes coated with a thin pellicle, which retards the evaporation to such an extent, that even after a fortnight's exposure the mass still continues to lose in weight; but by that time, however carefully the air was excluded, the base has partly been converted into carbonate. Some similar experiments, made in the amyl-series, which I shall describe in another part of this paper, have been attended with more success. From these experiments it may be inferred by analogy, that the residue remaining on evaporating a solution of oxide of tetrethylammonium is the hydrate

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} NO,\,HO$$

corresponding to hydrate of potassa. The hair-like crystals contain evidently in addition several equivalents of water of crystallisation; they may possibly be analogous to the well-known crystallised hydrate of potassa KO, HO + 4 Aq, which is formed at low temperatures.

It was above stated that the residuary substance left on evaporating a solution of the oxide of tetrethylammonium is decomposed, even at the temperature of boiling water. During this change a powerful ammoniacal odour is evolved, the substance strongly intumesces, and

is by degrees perfectly volatilised. If this process be conducted in an appropriate apparatus, it is found that the base, under these circumstances, yields three products of decomposition, namely, water, a highly alkaline oil, rather soluble in water, and a colourless inflammable gas. The oily base has all the properties of triethylamine; it was identified moreover by the analysis of its characteristic platinum-salt.

The inflammable gas evolved was pure olefiant gas; it was perfectly absorbed by bromine-water, proving the absence of hydrocarbons not belonging to the family $C_n H_n$, and the oily liquid formed had all the properties of the Dutch liquid. It readily solidified into a crystalline mass when exposed to a freezing mixture, a deportment whereby the olefiant gas compound may be easily distinguished from the corresponding compounds of propylene, butylene and amylene.

Hence the metamorphosis of oxide of tetrethylammonium under the influence of heat is represented by the following equation:—

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} NO,\,HO = 2\,HO + \left\{\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N + C_4\,H_4.$$

This change is not only interesting as an additional corroboration of the formula of the base, but likewise as affording a new source from which triethylamine may be obtained in a state of perfect purity, for as I shall show presently, the oxide may be also prepared from very impure mixtures of the lower ethyl-bases, and even from ammonia directly.

I have prepared several of the salts of tetrethylammonium. The sulphate, the nitrate, the phosphate, the carbonate, the hydrochlorate and the hydrobromate, all crystallize. But these salts are extremely soluble, and, with the exception of the carbonate, deliquescent, and but little adapted to analysis. They may be obtained either by directly saturating the oxide with the respective acids, or by double decomposition. The phosphate is conveniently prepared by gently heating a solution of the iodide with an excess of phosphate of silver, when, according to the silver-salt employed, either the common phosphate, or the pyrophosphate, &c. may be obtained. The phosphate thus obtained is strongly alkaline, like the tribasic soda-salt.

Tetrethylammonium forms a great number of beautiful double salts, of which I have examined a few.

Platinum-salt.—On adding a solution of bichloride of platinum to the chloride, an orange-yellow precipitate appears at once, which in every respect resembles the corresponding potassium- or ammonium-compound.

Like the latter it is slightly soluble in water, and less so in alcohol

and in ether; like the latter it may be crystallised in beautiful octohedrons, which contains

$$C_{16}\,H_{20}\,N\,Cl,\,Pt\,Cl_2 = \left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,Cl,\,Pt\,Cl_2.$$

Gold-Salt.—It is formed by mixing the solution of the two chlorides, when a lemon-yellow precipitate takes place, which is but slightly soluble in cold water or hydrochloric acid.

Formula

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,Cl, Au\,Cl_3.$$

Mercury-Salts.—a. *Chlorine-Compound.*—On adding an excess of protochloride of mercury to a nearly neutral solution of the chloride, a beautiful crystalline white precipitate is formed, which is soluble in water and in hydrochloric acid, especially on ebullition. From the boiling solution it is deposited on cooling in plates of a greasy appearance.

Formula

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,Cl,\ 5Hg\,Cl.$$

This somewhat peculiar composition, though chloride of mercury is known to join other compounds in rather unusual proportions, induced me to prepare an analogous iodine-compound, which on analysis was found to have a corresponding formula.

b. *Iodine-Compound.* — This substance was prepared in two different ways. Protiodide of mercury, when boiled with a solution of iodide of tetrethylammonium, loses at once its red colour, and is converted into a yellow compound, which fuses and collects as a transparent layer at the bottom of the vessel. On cooling it solidifies to a brittle mass, with crystalline fracture. The same substance is obtained by adding a large excess of protochloride of mercury to a solution of iodide of tetrethylammonium. A whitish crystalline precipitate is produced, which consists of a mixture of the double salt just mentioned, with a large amount of the corresponding chlorine-compound. By boiling with water the latter is removed, the former remaining behind.

Formula

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,I,\ 5Hg\,I.$$

The new oxide forms several other double compounds; but as their analysis would have scarcely given additional elucidation to the subject, I have omitted to study them in detail.

It now remained only to submit the new base again to the action of iodide of ethyl. An experiment on a small scale showed that the two compounds do not fail to act promptly upon one another. The mixture, after an hour's ebullition in a sealed tube, solidified into a beautiful crystalline mass. In order to obtain a precise notion of this reaction, I repeated this experiment upon a grand scale. Two ounces of iodide of tetrethylammonium were caustified by protoxide of silver, and then submitted to the action of about half a pound of iodide of ethyl. The mixture was kept boiling in a glass flask, provided with a long tube, in which the volatilised substances were condensed and returned to the seat of the reaction. During the whole process not a trace of permanent gas was disengaged. After a day's ebullition the solution had become neutral, and deposited on cooling magnificent crystals of iodide of tetrethylammonium, which were identified by analysis. On submitting the mother-liquor of the crystals to distillation in such a manner as to collect only the most volatile products, a considerable amount of perfectly pure alcohol was obtained, which was identified by a careful comparison of all its properties. The action of iodide of ethyl upon oxide of tetrethylammonium is therefore represented by the following equation—

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N, O, HO + C_4H_5I = C_4H_5O, HO + \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} NI.$$

I have since found that metallic oxides, such as protoxide of silver, in the presence of water, all exert the same action on iodide of ethyl; in this case a metallic iodide is formed, alcohol being reproduced.

The experiment just described shows that, as might have been expected, the ethylation cannot be carried on *ad infinitum*, and that the oxide of tetrethylammonium is the highest term attainable in the ethyl-series. The latter substance continues to act upon iodide of ethyl, but the change affects solely the iodide of ethyl, while the base is no longer altered.

ACTION OF IODIDE OF METHYL UPON TRIETHYLAMINE.

A mixture of triethylamine and iodide of methyl solidifies, after some time, to a crystalline mass, even at the common temperature. On ebullition the change takes place instantaneously. The crystalline compound thus produced may be viewed as the iodide of an organic metal, containing, together with nitrogen, one equivalent of methyl, and three of ethyl.

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N + C_2\,H_3\,I = \left\{\begin{matrix} C_2\,H_3 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,I.$$

In accordance with the nomenclature I have proposed for the preceding substance, this compound may be called iodide of methylotriethylammonium. And here is perhaps the place to ask for indulgence for the *sesquipedalia verba*, which I am using in the account of this investigation, and of which the worst, I fear, are still to come. However, the use of these barbarous names has the advantage of conveying an idea of the composition of the substances under examination in the shortest and most impressive manner. Moreover, none of these names are likely to remain in science; all these substances, which are prepared solely for the elucidation of a principle, will be forgotten as soon as the object is gained; they resemble paving-stones, each of which is very important in laying down a street, though no interest is attached to the blocks themselves, as soon as we are passing along the level road.

Iodide of methylotriethylammonium has all the properties which I have enumerated when speaking of the preceding compound. It is extremely soluble, forming a perfectly neutral, very bitter solution. On adding potassa to this solution, a heavy oily liquid is precipitated, which gradually solidifies. This is the unchanged iodide, which, like the corresponding tetrethylammonium-compound, is less soluble in alkaline solutions than in water. The iodide is readily decomposed by protoxide of silver, whereby the oxide is obtained in solution, which is caustic and bitter in the extreme. *In vacuo* it dries up to a crystalline compound, analogous to oxide of tetrethylammonium, the properties of which present the same difficulties to analysis. I have fixed the composition of this compound by the analysis of the beautiful platinum-precipitate, which is formed on adding the bichloride to a solution of the base saturated with hydrochloric acid.

It has the formula

$$C_{14}\,H_{18}\,N\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix} C_2\,H_3 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,Cl,\,Pt\,Cl_2.$$

I have not studied this substance very minutely; it forms crystalline salts with sulphuric, nitric, oxalic and hydrochloric acids.

ACTION OF IODIDE OF AMYL UPON TRIETHYLAMINE.

The experiment was conducted in a perfectly similar manner, and the results obtained are perfectly analogous. The action, however, is by no means so rapid as in the preceding cases, the amyl-sub-

stances being invariably much more inert than the corresponding terms in the ethyl- and methyl-series. In order to complete the process, it is necessary to heat the mixture in sealed tubes for two or three days. The iodide of amylotriethylammonium, for this is the new compound, forms remarkably fine crystals, which exhibit the fatty lustre and touch peculiar to the amyl-compounds. It is extremely soluble in water and alcohol, and insoluble in ether. The solutions have the bitter taste of quinine. On adding potassa or carbonate of potassa, the iodide separates as an oil, which rapidly shoots into brilliant needles. The salt when slightly moist fuses at 100° C. to a clear oily liquid, which becomes solid on cooling and perfect desiccation, and gradually assumes a yellow tint.

Its formula is

$$C_{22}\,H_{26}\,N\,I = \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N\,I.$$

When boiled with protoxide of silver the base is liberated and dissolves, forming an alkaline liquid of extremely bitter taste. The alkaline properties are however less marked than in the preceding bases. On evaporation the oxide of amylotriethylammonium remains in form of a syrup, which I have never seen assuming the crystalline form, perhaps because I have not allowed it to stand for a sufficiently long time. The sulphate and oxalate of this base, when evaporated in the bell of the air-pump, leave a syrupy or gummy residue like the base itself. The nitrate, however, and the hydrochlorate form beautiful crystals, the former hard, permanent needles of a cooling taste, the latter, leaves which are extremely deliquescent. The solution of the hydrochlorate is not precipitated by bichloride of platinum unless very concentrated. The salt once formed, however, is far less soluble. From a boiling solution in water it shoots into most magnificent orange-yellow needles, sometimes half an inch in length, which have the composition

$$C_{22}\,H_{26}\,N\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N\,Cl,\,Pt\,Cl_2.$$

The remarkable change exhibited by oxide of tetrethylammonium, when submitted to the action of heat, necessarily induced me to study the deportment of the amylotriethylated base under similar circumstances. This study appeared to promise some farther revelations respecting the molecular constitution of this body, a hope in which I was not deceived. I had no doubt in my mind that the process alluded to would give rise to the formation of a nitrile-base, but

there were two alternatives which presented themselves as to the nature of this base. The question arose: Will an equivalent of ethyl or amyl be broken up in this decomposition? This question had to be decided by experiment.

ACTION OF HEAT ON OXIDE OF AMYLOTRIETHYLAMMONIUM.

Oxide of amylotriethylammonium, when subjected to distillation, begins to froth as soon as the solution becomes concentrated, after which decomposition rapidly sets in. The products of this decomposition are water, an oily substance, and a transparent inflammable gas. The latter, by the method I have indicated when speaking of the decomposition of oxide of tetrethylammonium, was proved to be perfectly pure olefiant gas, when the composition of the oily liquid was no longer doubtful. It was evident that this substance must be a nitrile-base containing two equivalents of ethyl and one equivalent of amyl.

$$\left.\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} NO,\ HO = 2HO + \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N + C_4\ H_4.$$

Experiment has entirely confirmed this view. Diethylamylamine—for this is the name which appertains to the new compound—has a peculiar, not unpleasant aromatic odour, and an analogous somewhat bitter taste, is lighter than water, in which it scarcely dissolves, imparting to it a slight but decided alkaline reaction. It combines with acids less readily than do the bases, which occupy a lower position in the system. The salts with sulphuric, nitric, oxalic and hydrochloric acids, crystallise beautifully, but are deliquescent. Diethylamylamine, when dried over hydrate of potassa and rectified, exhibits a perfectly constant boiling-point at 154° C.

I have fixed the composition of this base, as usual, by the analysis of the platinum-salt. This compound is obtained by concentrating a mixture of the hydrochlorate with bichloride of platinum, when it shoots into long magnificent orange-yellow prisms. It contains:

$$C_{18}\ H_{21}\ N,\ HCl,\ Pt\ Cl_2 = \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{10}\ H_{11} \end{matrix}\right\} N,\ H\ Cl,\ Pt\ Cl_2.$$

The formula of diethylamylamine is unequivocally supported by the boiling-point. This compound differs from diethylamine by $C_{18}\ H_{21}\ N - C_8\ H_{11}\ N = C_{10}\ H_{10} = 5C_2\ H_2$. I have lately prepared diethylamine on a larger scale, and found its boiling-point to be 57° C.; on starting from this number the boiling-point of diethyl-

amylamine should be $57+(5\times19)=152°$. The experimental boiling-point is 154°.

Having seen by the preceding experiments that ethyl, as it were, yields its place to amyl, the idea naturally suggested itself to inquire into the mutual relations of ethyl and methyl under similar circumstances. For this purpose I might have studied the action of heat upon oxide of methylotriethylammonium; however, as I had some grammes of diethylamylamine at my disposal, I preferred to methylate this compound, and examine the new body thus obtained.

ACTION OF IODIDE OF METHYL UPON DIETHYLAMYLAMINE.

On adding iodide of methyl to diethylamylamine, the phenomena which I have already several times described are repeated in turn. The action in this case, however, is so violent that the iodide must be added very gradually, for on suddenly mixing, the liquid is projected from the vessel with a sort of explosion; on account of the low boiling-point of the methyl-compound, it is advisable to mix in a tubulated retort provided with a condenser.

On cooling the mixture solidifies into a hard white crystalline mass, consisting of a new iodide, for which, in accordance with the nomenclature which I have adopted, I propose the name iodide of methylodiethylamylammonium.

$$\left.\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}N+C_2\ H_3\ I=\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}N\ I.$$

The new iodide, like the preceding analogues, is extremely soluble in water, forming a very bitter solution, from which it is reprecipitated by potassa in oily globules, which solidify again but slowly.

When digested with protoxide of silver, the iodide yields the oxide in form of a powerful alkaline solution, which forms crystalline salts with sulphuric, nitric and hydrochloric acid. The hydrochlorate of methylodiethylamylammonium gives with bichloride of platinum a beautiful salt, having the formula

$$C_{20}\ H_{24}\ N\ Cl,\ Pt\ Cl_2=\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}N\ Cl,\ Pt\ Cl_2.$$

ACTION OF HEAT UPON OXIDE OF METHYLODIETHYLAMYLAMMONIUM.

When submitted to distillation this compound is decomposed like the analogous substances, the product being water, pure olefiant gas,

which was identified as formerly, and a very remarkable nitrile-base, containing the three different alcohol radicals, an ammonia, in fact, in which the first equiv. of hydrogen is replaced by methyl, the second by ethyl, the third by amyl, and which receives the name methylethylamylamine.

$$\left.\begin{matrix} C_2 & H_3 \\ C_4 & H_5 \\ C_4 & H_5 \\ C_{10} & H_{11} \end{matrix}\right\} NO, HO = 2HO + \left\{\begin{matrix} C_2 & H_3 \\ C_4 & H_5 \\ C_{10} & H_{11} \end{matrix}\right\} N + C_4H_4.$$

This reaction shows that ethyl yields its place even to methyl, a fact which could not have been anticipated from analogy, methyl occupying a lower position than ethyl in the system. The above deportment is moreover remarkable, when considered in another point of view. The elimination of methyl in the case under examination would have given rise to the formation of methylene C_2H_2, a substance the existence of which is still very problematical.

Methylethylamylamine is a transparent oil of a fragrant odour and an analogous taste. Both these properties are much more marked than those of diethylamylamine, which it resembles in most respects. It is somewhat more soluble in water than the latter, and of a more decided alkaline character. When dried over potassa and rectified, the new base boils constantly at 135°. Hence its boiling-point is $154-135=19°$ lower than that of diethylamylamine, a difference which is in perfect accordance with H. Kopp's rule.

Methylethylamylamine dissolves but slowly in the acids, forming salts which resemble those of the diethylamylated base. The hydrochlorate gives with bichloride of platinum a beautiful double salt, which is extremely soluble in water. It is usually precipitated on mixing the highly concentrated solutions, or on evaporating the mixture, in oily globules of a deep orange-yellow, which gradually solidify into magnificent needles, containing

$$C_{16}\ H_{19}\ N,\ H\ Cl,\ Pt\ Cl_2 = \left\{\begin{matrix} C_2 & H_3 \\ C_4 & H_5 \\ C_{10} & H_{11} \end{matrix}\right\} N,\ H\ Cl,\ Pt\ Cl_2.$$

In the preceding experiments, the radicals of the alcohols $C_n\ H_{(n+2)}\ O_2$ have been exclusively used as replacing materials. However, as might have been expected, nitrile-bases containing a radical which is not homologous but only analogous to the two others, exhibit a deportment exactly similar when submitted to the action of iodide of methyl, of ethyl or of amyl. In order to establish this point, I had to return once more to the aniline-series.

ACTION OF IODIDE OF ETHYL UPON DIETHYLANILINE.

In my former paper* I have recorded a few experiments on the action of bromide of ethyl upon diethylaniline. The results, unintelligible to me at that period, are now perfectly clear. I have since repeated these reactions, substituting the iodide for the bromide on account of its more prompt action. Diethylaniline is perfectly soluble in iodide of ethyl; on exposing the mixture, sealed in tubes, to the temperature of boiling water, the liquid column gradually separates into two layers, the lower one increasing in bulk with the time of exposure, and solidifying on cooling into a semi-solid crystalline mass. The reaction is terminated when, after half a day's ebullition, the volume of the lower layer, which is the new iodide in the fused state, ceases to increase.

The mixture is now distilled with water in order to separate an excess of either diethylaniline or iodide of ethyl, when a strongly acid solution of iodide of phenylotriethylammonium is obtained, which usually contains a small quantity of hydriodate of diethylaniline, as may be inferred from the oily precipitate produced in the solution by potassa, which does not redissolve on addition of more water.

Digestion with protoxide of silver separates the two bases, one of which, diethylaniline, being insoluble in water, remains mixed with the oxide and iodide of silver, the other, the oxide of phenylotriethylammonium, forming a powerfully alkaline solution of a strongly bitter taste.

After having ascertained by treatment with ether that the solution did not retain a trace of diethylaniline, it was saturated with hydrochloric acid and mixed with bichloride of platinum, when at once a pale-yellow, apparently amorphous precipitate was thrown down, which was scarcely soluble in water and insoluble in alcohol and ether.

Formula

$$C_{24}\,H_{20}\,N\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_{12}\ H_5 \end{matrix}\right\} N\,Cl,\,Pt\,Cl_2.$$

I have not examined any farther the compounds of this base; I have only ascertained that the sulphate, nitrate, oxalate and hydrochlorate crystallise, although with difficulty.

When oxide of phenylotriethylammonium is submitted to the action of heat, it yields, as might have been expected, water, olefiant gas and diethylophenylamine (diethylaniline).

* Philosophical Transactions, 1850, Part I. p. 107.

$$\left.\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_4\ H_5 \\ C_{12}\ H_5 \end{matrix}\right\} NO,\ HO = 2HO + \left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{12}\ H_5 \end{matrix}\right\} N + C_4\ H_4.$$

ACTION OF IODIDE OF METHYL UPON ETHYLAMYLANILINE.

Ethylamylaniline, which I formerly obtained* by the action of bromide of amyl upon ethylaniline, or of bromide of ethyl upon amylaniline, may be formed with the same, or greater facility, by exposing the latter base to iodide of ethyl. When submitted to the action of iodide of methyl at the temperature of boiling water for three or four days, ethylamylaniline exhibits all the phenomena described in the preceding paragraph. The lower layer, which solidifies, is a mixture of hydriodate of ethylamylaniline and iodide of methylethylamylophenylammonium. *Sit venia verbo !*

$$\left.\begin{matrix} C_4\ H_5 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N + C_2\ H_3\ I = \left\{\begin{matrix} C_2\ H_3 \\ C_4\ H_5 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N\ I.$$

The corresponding oxide is obtained as the preceding one, namely, by treating the clear solution of the two iodine-compounds, previously freed by ebullition from an excess of iodide of methyl, or ethylamylaniline, with protoxide of silver, when unchanged ethylamylaniline and the base with the long name separate. The latter remaining in solution (and forming a very bitter liquid of a strongly alkaline reaction,) whilst the former is insoluble, there was no difficulty in obtaining a pure platinum-salt whereby to prove the composition of the compound in question. This salt is a pale-yellow amorphous precipitate, very soluble in water, and has the composition

$$C_{28}\ H_{24}\ N\ Cl,\ Pt\ Cl_2 = \left\{\begin{matrix} C_2\ H_3 \\ C_4\ H_5 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N\ Cl,\ Pt\ Cl_2.$$

This compound is certainly remarkable for the diversity of its components, for it contains the radicals of not less than four different alcohols !

As to the action of heat upon the oxide under examination, there could be scarcely any doubt after the result of the preceding investigation. Still I have established by experiment that in this reaction olefiant gas is eliminated, whilst a new nitrile-base, containing methyl, amyl and phenyl, is generated.

* Philosophical Transactions, 1850, Part I. p. 117.

$$\left.\begin{matrix} C_2\ H_3 \\ C_4\ H_5 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N\,O,\ HO = 2HO + \left\{\begin{matrix} C_2\ H_3 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N + C_4\ H_4.$$

Methylamylophenylamine is an oil of an odour similar to that of amylaniline; it is almost insoluble in water: I have not prepared enough of this compound to determine the boiling-point, which at all events is very high. It forms a crystalline platinum-salt, whose analysis led to the formula

$$C_{24}\ H_{19}\ N,\ H\ Cl,\ Pt\ Cl_2 = \left\{\begin{matrix} C_2\ H_3 \\ C_{10}\ H_{11} \\ C_{12}\ H_5 \end{matrix}\right\} N,\ H\ Cl,\ Pt\ Cl_2,$$

Bases of the Methyl-series.

ACTION OF AMMONIA UPON IODIDE OF METHYL.

If iodide of methyl be treated with a concentrated aqueous solution of ammonia, the former is rapidly dissolved, the completion of the reaction being indicated by the liquid assuming a yellowish tint. On opening the boiler-tube the liquid is found to be strongly acid, and to contain not less than five different iodides, namely—

Iodide of Ammonium . . . . . $\left\{\begin{matrix} H \\ H \\ H \\ H \end{matrix}\right\} N\,I.$

Iodide of Methylammonium . . . . . $\left\{\begin{matrix} H \\ H \\ H \\ C_2\ H_3 \end{matrix}\right\} N\,I.$

Iodide of Dimethylammonium . . . . . $\left\{\begin{matrix} H \\ H \\ C_2\ H_3 \\ C_2\ H_3 \end{matrix}\right\} N\,I.$

Iodide of Trimethylammonium . . . . . $\left\{\begin{matrix} H \\ C_2\ H_3 \\ C_2\ H_3 \\ C_2\ H_3 \end{matrix}\right\} N\,I.$

Iodide of Tetramethylammonium . . . . $\left\{\begin{matrix} C_2\ H_3 \\ C_2\ H_3 \\ C_2\ H_3 \\ C_2\ H_3 \end{matrix}\right\} N\,I.$

Of these five compounds, the first and the last are formed in considerable excess. Of the remainder I have as yet only been able

to establish the presence of the iodide of methylammonium by numbers. The two others I have not as yet obtained in sufficiently large quantity and of the requisite purity. The solution of this mixture deposits, on cooling, magnificent dazzling-white hard flat needles, sometimes of an inch in length, which are very difficultly soluble in cold water, and may be obtained in the state of purity by washing with cold and recrystallising from boiling water. These crystals are the iodide of tetramethylammonium, all the other salts remaining in the mother-liquor, which rapidly turns brown on exposure to the atmosphere. The facility with which ammonia acts upon iodide of methyl, renders it unnecessary to perform the process at a high temperature. The reaction is accomplished after some days, even at the common temperature, if an alcoholic solution be employed, after some hours, a considerable amount of heat being disengaged.

Iodide of Tetramethylammonium.

This substance possesses the family-features of the group. It is soluble in water, but far less so than the corresponding ethyl-compound, forming a perfectly neutral solution of an extremely bitter taste. It is almost insoluble in absolute alcohol, insoluble in ether. Like the ethyl-compound, this salt is far less soluble in potassa than in pure water.

It has the following formula:

$$C_8 H_{12} N I = \left\{ \begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix} \right\} N I.$$

The action of protoxide of silver upon the iodine-compound is perfectly analogous to that which it exerts upon the ethyl-body. The oxide of tetramethylammonium thus liberated is endowed with scarcely less marked properties than the ethyl-base. When evaporated over sulphuric acid *in vacuo*, it likewise dries up to a crystalline mass, attracting moisture and carbonic acid with the greatest avidity; saturated with acids, it yields crystallisable salts. I have prepared the sulphate, oxalate, nitrate and hydrochlorate; the nitrate especially crystallises well, in long brilliant needles.

The hydrochlorate yields with bichloride of platinum a magnificent double salt, which is less insoluble than the corresponding salt in the ethyl-series; it crystallises in perfectly regular octohedrons of a deep-orange colour, which have the formula,

$$C_8 H_{12} N Cl, Pt Cl_2 = \left\{ \begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix} \right\} N Cl, Pt Cl_2:$$

I was exceedingly desirous to submit this oxide to the action of heat; for this process, provided the methyl-base followed the deportment of its ethyl-fellow, promised to give me the long desired methylene $C_2 H_2$. Oxide of tetramethylammonium, when heated, violently intumesces, and is completely volatilised; the product of the distillation is an extremely volatile and powerfully alkaline liquid; but strange to say, during the whole process not a trace of gas is disengaged. I have repeatedly performed the experiment with exactly the same result. Here then we meet with a new mode of decomposition, and unless I am much mistaken, with a decomposition of a very peculiar character. I have made a few experiments with the basic liquid disengaged, but as I have not as yet arrived at perfectly definite results, I refrain from entering into farther details.

The mother-liquor of iodide of tetramethylammonium, which contains chiefly iodide of ammonium, together with small quantities of the intermediate iodides, yields all the corresponding bases by distillation with potassa. However, the ammonia prevails in the distillate to such an extent, that the attempt to effect a separation would have been hopeless. It was only by precipitating the liquid with bichloride of platinum, and separating the more soluble from the less soluble salts, that I succeeded in obtaining evidence of the presence of the intermediate bases. As yet I have been able to prepare only the methylamine-salt in a state of tolerable purity.

Bases of the Amyl-series.

Amylamine.

Ammonia acts but very slowly upon iodide of amyl, and the product of the reaction contains, as in the methyl-series, not less than five iodides. Among these the iodides of amylammonium and diamylammonium are present in the smallest quantity. The preparation of amylamine succeeds much better according to the process of M. Wurtz, namely, by submitting cyanate of amyl to the action of hydrate of potassa.

ACTION OF BROMIDE OF AMYL UPON AMYLAMINE.

Diamylamine.

The formation of diamylamine takes place even in the cold, although slowly. At the temperature of boiling water, a mixture of amylamine and bromide of amyl is rapidly converted into a beautiful white crystalline mass of hydrobromate of diamylamine, which is purified, and decomposed in the usual manner. When purified, diamylamine is a light oily substance, very little soluble in water, to

which it imparts, however, an alkaline reaction. Its aromatic odour is peculiar, not unpleasant, and reminds us of amylamine; its taste hot and pungent; it boils at about 170°. From want of pure material, the boiling-point could not be determined with accuracy.

Diamylamine forms very beautiful crystalline salts with the acids, which are all rather insoluble in water. The hydrochlorate is almost insoluble in cold water, but may be recrystallised from boiling water. This solution yields with bichloride of platinum a double salt, which is rather soluble, and separates frequently, in the first instance, in the form of oily drops, which become gradually crystalline.

The former has the formula

$$C_{20}\,H_{23}\,N,\,H\,Cl = \left\{\begin{matrix} H \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N,\,H\,Cl$$

The latter has the formula

$$C_{20}\,H_{23}\,N,\,H\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix} H \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N,\,H\,Cl,\,Pt\,Cl_2.$$

ACTION OF BROMIDE OF AMYL UPON DIAMYLAMINE.

Triamylamine.

This base arises from diamylamine in the same manner as the latter from amylamine. It is moreover obtained, and at once in a state of purity, by exposing oxide of tetramylammonium, which I shall describe presently, to a high temperature; prepared by either way, this substance resembles in most of its physical and chemical characters diamylamine; it boils, however, at a much higher temperature, namely, at 257°. Its composition was fixed as that of diamylamine, by the analysis of the hydrochlorate and of the platinum-salt, the former being a very characteristic salt, which separates at once in nacreous plates on adding hydrochloric acid to the base, the latter being a viscid salt gradually solidifying to a crystalline mass.

The hydrochlorate contains

$$C_{30}\,H_{33}\,N,\,H\,Cl = \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N,\,H\,Cl$$

The latter

$$C_{30}\,H_{33}\,N,\,H\,Cl,\,Pt\,Cl_2 = \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N,\,H\,Cl,\,Pt\,Cl_2.$$

ACTION OF IODIDE OF AMYL UPON AMYLAMINE AND UPON AMMONIA.

Oxide of Tetramylammonium.

A mixture of triamylamine and iodide of amyl solidifies after two or three days' ebullition to a solid, somewhat fat-like mass of iodide of tetramylammonium. A similar effect is produced by boiling an excess of iodide of amyl with a concentrated solution of ammonia. This reaction, however, takes place very slowly; in fact, the diminution of affinities characterising the amyl-compounds in general was in none of these cases more marked. After two or three days' ebullition the volume of the ether appeared scarcely diminished; but then a gradual change occurred, the heavy amyl-compound rising and floating upon the solution of the new iodide which was formed. After a fortnight's ebullition the aqueous layer began to solidify, when allowed to cool; but even after keeping the mixture for a period of three weeks in ebullition, on opening the boiler-tube the reaction was found to be far from complete.

The semi-solid mixture thus obtained was subjected to distillation, first alone, in order to recover the iodide of amyl not acted upon; then with potassa, to separate ammonia and the lower amyl-bases. The alkaline liquid contained a small quantity of iodide of tetramylammonium in solution, which crystallised on cooling in fat-like leaves; the larger quantity, however, of this substance collected at the bottom of the vessel in form of a heavy oil, which solidified on cooling to a hard mass of the appearance of stearin.

The new iodide resembles in its general properties the corresponding compounds I have previously described. Like them it is soluble, but only with difficulty, in water, forming a most intensely bitter liquid, and reprecipitated from this solution in the crystalline form by the addition of the alkalies. On drying, the iodide assumes a slightly yellowish tint.

The formula of this compound is

$$C_{40}\,H_{44}\,N\,I = \left\{\begin{matrix} C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \\ C_{10}\,H_{11} \end{matrix}\right\} N\,I.$$

On boiling the iodide with protoxide of silver, an alkaline, very bitter solution of the oxide of tetramylammonium is obtained. This substance is evidently far less soluble in water than the corresponding bases in the methyl- and ethyl-series. It would almost appear as if

this compound stood to the methyl- and ethyl-bases as an alkaline earth does to potassa and soda.

On adding potassa to a solution of oxide of tetramylammonium, the base rises in the form of an oily layer on the surface of the liquid. The same separation is observed when the solution is much evaporated; in the latter case the oily layer gradually solidifies. On allowing a moderately concentrated solution of this base to stand for some time in a vessel in which it is protected from carbonic acid, magnificent perfectly definite crystals, sometimes an inch in length and in thickness, are deposited; they are but moderately deliquescent, and attract carbonic acid from the air but slowly. These crystals are the hydrate of tetramylammonium, containing a certain amount of water of crystallisation. I have not yet been able to determine the number of equivalents. On heating these crystals, they fuse in their water of crystallisation, and yield on evaporation in the water-bath a viscid semi-solid transparent mass, which is the hydrated oxide of tetramylammonium,

$$\left.\begin{matrix} C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \end{matrix}\right\} N\,O,\ HO.$$

The oxide, when heated in the water-bath, yields a small quantity of triamylamine. At a higher temperature this reaction proceeds with perfect regularity; an inflammable carbohydrogen being disengaged, together with the base. There can be scarcely any doubt that the former is amylene. This substance boils at a rather low temperature, 39°, and was therefore partly collected as gas. Another portion, however, dissolved in the triamylamine, from which it was expelled by ebullition after the base had been fixed by addition of hydrochloric acid. Hence the decomposition of oxide of tetramylammonium is perfectly analogous to that of its analogues in the ethyl-series, and is represented by the equation

$$\left.\begin{matrix} C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \end{matrix}\right\} NO,\ HO = 2HO + \left\{\begin{matrix} C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \end{matrix}\right\} N + C_{10}\ H_{10}.$$

Oxide of tetramylammonium is distinguished by forming crystalline salts of remarkable beauty. The sulphate crystallises in long hair-like filaments, the nitrate in needles, the oxalate in splendid large perfectly-defined plates, of a very bitter taste, and extremely deliquescent. The chloride crystallises in leaves with palm-like ramifications; it is likewise deliquescent, but less so than the preceding

salt. The solution of the chloride yields with bichloride of platinum a pale-yellow curdy precipitate, which gradually solidifies into beautiful orange-yellow needles, of the composition

$$C_{40}\ H_{44}\ N\ Cl,\ Pt\ Cl_2 = \left\{\begin{matrix} C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \\ C_{10}\ H_{11} \end{matrix}\right\} N\ Cl,\ Pt\ Cl_2.$$

Before passing on to some general considerations, which the experiments detailed in the preceding paper suggest, it appears to be desirable to condense the whole of the materials into a synoptical form. The appended table requires no commentary; it contains the formulæ of the alkaloids described in this and the preceding memoir, exhibiting in a clear light the arrangement of the molecules composing them, and the manner in which the various compounds are interchained.

TYPE.	AMIDOGEN-BASES.	IMIDOGEN-BASES.	NITRILE-BASES.	ANALOGUES OF OXIDE OF AMMONIUM.
Ammonia (Amine) $\left\{\begin{matrix}H\\H\\H\end{matrix}\right\}$ N.	Aniline (Phenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\ H_5\end{matrix}\right\}$ N.	Ethylaniline (Ethylophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.	Diethylaniline (Diethylophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.	Oxide of Triethylophenylammonium $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ NO, HO.
		Methylaniline (Methylophenylamine) $\left\{\begin{matrix}H\\C_2\ H_3\\C_{12}\ H_5\end{matrix}\right\}$ N.	Methylethylaniline (Methylethylophenylamine) $\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.	
		Amylaniline (Amylophenylamine) $\left\{\begin{matrix}H\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.	Diamylaniline (Diamylophenylamine) $\left\{\begin{matrix}C_{10}\ H_{11}\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.	
			Ethylamylaniline (Ethylamylophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.	
			Methylamylamine (Methylamylophenylamine) $\left\{\begin{matrix}C_2\ H_3\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.	Oxide of Methylethylamylophenylammonium $\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ NO, HO.
	Chloraniline (Chlorophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\ (H_4\ Cl)\end{matrix}\right\}$ N.	Ethylochloraniline (Ethylochlorophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\ (H_4\ Cl)\end{matrix}\right\}$ N.	Diethylochloraniline (Diethylochlorophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{12}\ (H_4\ Cl)\end{matrix}\right\}$ N.	
	Bromaniline (Bromophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\ (H_4\ Br)\end{matrix}\right\}$ N.	Ethylobromaniline (Ethylobromophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\ (H_4\ Br)\end{matrix}\right\}$ N.		
	Nitraniline (Nitrophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\ (H_4\ NO_4)\end{matrix}\right\}$ N.	Ethylonitraniline (Ethylonitrophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\ (H_4\ NO_4)\end{matrix}\right\}$ N.		
	Ethylamine (Ethylammonia) $\left\{\begin{matrix}H\\H\\C_4\ H_5\end{matrix}\right\}$ N.	Diethylamine (Diethylammonia) $\left\{\begin{matrix}H\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}$ N.	Triethylamine (Triethylammonia) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}$ N.	Oxide of Tetrethylammonium $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}$ NO, HO.
			Diethylamylamine (Diethylamylammonia) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}$ N.	Oxide of Triethylamylammonium $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}$ NO, HO.
				Oxide of Triethylomethylammonium $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\\C_2\ H_3\end{matrix}\right\}$ NO, HO.
			Methylethylamylamine (Methylethylamylammonia) $\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}$ N.	Oxide of Diethylomethylamylammonium $\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_4\ H_5\\C_{10}\ H_{11}\end{matrix}\right\}$ NO, HO.
	Methylamine (Methylammonia) $\left\{\begin{matrix}H\\H\\C_2\ H_3\end{matrix}\right\}$ N.	Dimethylamine (Dimethylammonia) $\left\{\begin{matrix}H\\C_2\ H_3\\C_2\ H_3\end{matrix}\right\}$ N.	Trimethylamine (Trimethylammonia) $\left\{\begin{matrix}C_2\ H_3\\C_2\ H_3\\C_2\ H_3\end{matrix}\right\}$ N.	Oxide of Tetramethylammonium $\left\{\begin{matrix}C_2\ H_3\\C_2\ H_3\\C_2\ H_3\\C_2\ H_3\end{matrix}\right\}$ NO, HO.
	Amylamine (Amylammonia) $\left\{\begin{matrix}H\\H\\C_{10}\ H_{11}\end{matrix}\right\}$ N.	Diamylamine (Diamylammonia) $\left\{\begin{matrix}H\\C_{10}\ H_{11}\\C_{10}\ H_{11}\end{matrix}\right\}$ N.	Triamylamine (Triamylammonia) $\left\{\begin{matrix}C_{10}\ H_{11}\\C_{10}\ H_{11}\\C_{10}\ H_{11}\end{matrix}\right\}$ N.	Oxide of Tetramylammonium $\left\{\begin{matrix}C_{10}\ H_{11}\\C_{10}\ H_{11}\\C_{10}\ H_{11}\\C_{10}\ H_{11}\end{matrix}\right\}$ NO, HO.

[*To face p.* 326.

The preceding researches show that the action of the bromides and iodides of the alcohol-radicals upon ammonia, gives rise to the formation of not less than four distinct groups of organic bases. Of these, the members of three groups, corresponding to ammonia (H_3 N), are volatile, while those of the fourth, corresponding to oxide of ammonium (H_4 N O), cannot be volatilised without decomposition. The facility with which the members of this last class arise from those of the preceding ones, and the readiness with which their reconversion is effected, renders the former group as it were the connecting link between the volatile and the non-volatile organic alkaloids. I am inclined to attach some importance to the latter point, for the acquisition of a general method, by means of which we may rise from the volatile to the non-volatile bases, is not unlikely to pave the way to the artificial production of the fixed native alkaloids, whose constitution is still shrouded in darkness. We may here remember that a very considerable number of these *fixed* native alkaloids yield *volatile* organic bases when submitted to the action of heat or of potassa,—that is, under precisely those conditions under which the new ammonium-compounds, which I have described in this paper, are converted into conjugate ammonias. Thus quinine, cinchonine, strychnine, and pelosine yield among their products of decomposition leucoline (chinoline), while piperine gives picoline (?), and morphine, caffeine, codeine and narcotine have actually been converted into alcohol-bases, the former yielding methylamine, the latter two, propylamine.*

I readily admit that those processes are by no means so simple as the passage of oxide of tetrethylammonium into triethylamine, several processes of transformation being in most of these cases accomplished side by side. A certain analogy, however, cannot possibly be denied, although, on account of the more complicated formulæ of the native

* M. Wertheim, the discoverer of this base, believes that it stands to the unknown propyl-alcohol in the same relation which exists between methylamine, ethylamine and amylamine on the one hand, and methylic, ethylic and amylic alcohols on the other. It deserves, however, to be noticed that the formula $C_6 H_9 N$ for this compound, as determined by experiment, expresses not only propylamine, but also trimethylamine and even methylethylamine.

$$C_6 H_9 N = \left\{ \begin{matrix} H \\ H \\ C_6 H_7 \end{matrix} \right\} N = \left\{ \begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix} \right\} N = \left\{ \begin{matrix} H \\ C_2 H_3 \\ C_4 H_5 \end{matrix} \right\} N.$$

In the absence of decisive reactions, it remains doubtful which of these formulæ represents the base obtained by the action of soda-lime on narcotine; I may state here that propylamine, as prepared by Wertheim's process, and the liquid containing trimethylamine, for as yet I have not obtained this substance perfectly pure, exhibit the same remarkable fishy odour. It deserves, moreover, to be remarked that Dr. Anderson found that propylamine occurs, associated with methylamine, among the basic products of the decomposition of codeine.

bases, it cannot as yet be traced in simple equations. In some instances the connection even now appears almost palpable. If we compare the formulæ of quinine and of leucoline, the volatile base derived from its destruction, we are surprised to find that these substances exhibit the same elementary difference which we observe between oxide of tetramethylammonium and trimethylamine.

$$\underbrace{C_{20}\,H_{12}\,N\,O_2}_{\text{Quinine.}} - C_2\,H_4\,O_2 = \underbrace{C_{18}\,H_8\,N}_{\text{Leucoline.}}$$

$$\underbrace{C_8\,H_{13}\,N\,O_2}_{\text{Hydrated oxide of Tetramethyl-ammonium.}} - C_2\,H_4\,O_2 = \underbrace{C_6\,H_9\,N}_{\text{Trimethyl-amine.}}$$

Accordingly, we might expect that the action of the iodide of methyl upon leucoline, and the subsequent decomposition of the iodide produced by means of protoxide of silver, would enable us to re-convert leucoline in this manner into quinine. This metamorphosis would be the more interesting, as it would open a source for the artificial production of quinine; leucoline being, as is well known, contained in considerable quantity in the basic portion of coal-tar-naphtha. It may be stated here that leucoline, which is a substance remarkable for its antipathy to the crystalline form, when submitted to the action of iodide of methyl, solidifies at once into a splendid mass of crystals of a new iodide,* which in fact resembles in its outward appearance hydriodate of quinine, and which is still under examination. I am, however, by no means sanguine as to the result of this experiment, for the above play of formulæ rests as yet on a very precarious foundation; neither the formula of quinine nor that of leucoline being established beyond a doubt. Nevertheless, I intend to complete this investigation, because even if no other result is obtained, yet by means of this process new data for ultimately fixing the formulæ of quinine and leucoline may be found.

* A similar result is obtained by the action of iodide of ethyl upon conine and nicotine.

The last part of the paper communicated to the Royal Society is devoted to the discussion how far the received views regarding the constitution of the ammonia-salts are affected by the preceding researches, and how far the ideas suggested by the above experiments are applicable to some very well known compounds of mineral chemistry. For the detail of these considerations I beg to refer to the original memoir.

On the Qualitative Distinction of Tin, Antimony and Arsenic.

By T. Fleitmann.*

An easy and expeditious method of distinguishing these metals, when associated together, being still a desideratum in analytical chemistry, the author proposes the following as a step towards the attainment of this object.

Tin and antimony, when they occur together, may be distinguished by the solubility of metallic tin in strong hydrochloric acid, and by the insolubility in hypochlorite of soda of the antimony spots obtained by Marsh's process.

When a piece of metallic zinc is immersed in a solution of tin and antimony, slightly acidulated with hydrochloric acid, both metals are precipitated; but a portion of the antimony is given off in the form of antimoniuretted hydrogen. If the precipitation be performed in a small apparatus, fitted up for disengaging hydrogen, the antimony may be easily detected by the black spots insoluble in hypochlorite of soda, which it produces on a porcelain dish. If the precipitated metallic powder of tin and antimony be afterwards boiled with strong hydrochloric acid only, the tin dissolves in the form of protochloride, which, after proper dilution with water, may be recognised by the brown precipitate which it forms with sulphuretted hydrogen (or the purple with chloride of gold). Neither of these reactions is at all modified by the presence of arsenic.

The recognition of arsenic in presence of antimony depends upon a remarkable difference which these metals exhibit in their behaviour with hydrogen, at the moment when the latter is set free from an alkaline liquid. When a strongly alkaline solution of antimony is heated in contact with metallic zinc, the antimony is precipitated, and pure hydrogen is rapidly evolved, without the slightest trace of

* Ann. Ch. Pharm. LXXVII, 126.

antimoniuretted hydrogen. On the contrary, when a substance containing arsenic acid is mixed with excess of potash and with zinc filings, and the liquid heated, hydrogen gas, strongly impregnated with arseniuretted hydrogen, is given off. The presence of the arseniuretted hydrogen is most easily recognised by holding a strip of paper, moistened with nitrate of silver, at a short distance above the liquid. The paper should be wrapped round a glass rod, inserted through a cork which fits into the mouth of the vessel. The smallest traces of arsenic produce a perceptible blackening.

The evolution of gas is unfortunately too slow to enable us to use Marsh's test in the ordinary way. This defect may be remedied by evolving pure hydrogen gas in another vessel, and passing it into the vessel containing the zinc and potash. In this manner, perceptible black spots may be produced, with a single drop of the solution of arsenious acid in hydrochloric acid, both in a porcelain plate, and by heating in a glass tube. But the process, thus modified, and deprived of its original simplicity, is decidedly inferior to that invented by Fresenius and Babo.

THE

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OF THE

CHEMICAL SOCIETY.

XXVI.—*Description of the Lapis Lazuli found in large quantities in the Cordilleras of the Andes.*

By F. Field, F.C.S.

The discovery of immense masses of a bright blue rock, in the Cordilleras, led a miner to suppose he had discovered a vein of the blue carbonate of copper. On analyzing a specimen, I found it to be perfectly destitute of that metal, and to be in fact a true lapis lazuli, interspersed with small veins of pure carbonate of lime. Heated by itself, it loses colour, but regains its primitive appearance on cooling; with nitre, on the application of the blow-pipe flame, it becomes highly incandescent, and of a most beautiful green. It dissolves in borax with lively effervescence, into a pure colourless glass, becoming slightly opalescent on cooling. On the addition of nitric acid, there is a brisk evolution of carbonic acid—the mineral becomes perfectly colourless, and presents a solid mass of gelatinous silica. The following is its composition in 100 parts. The analysis offered no difficulties:

Silica	37·60
Alumina	11·21
Sulphur	1·65
Iron	0·08
Magnesia	0·36
Soda	9·66
Carbonic acid	15·05
Lime	24·10
	99·71

This probably is not exactly the proper expression of its constitution, the sulphur no doubt being in combination with a portion of the sodium from the soda, as well as with iron. That the sulphur exists *as such*, and not in the state of sulphuric acid, is evident by the addition of acetic acid, which causes a strong disengagement of sulphuretted hydrogen, and in the residue no trace of sulphur can be detected by solution, and addition of a salt of baryta. I believe the colour of the stone is usually attributed to minute portions of sulphide of iron and sodium. Gmelin, however, in an analysis of lapis lazuli, places all the sulphur as sulphuric acid. (See Chapman's Mineralogy, p. 81.)

XXVII.—*Analysis of a Mineral containing Gold, from the Province of Coquimbo, Chili.*

By F. Field, F.C.S.

The mineral about to be described is very similar to various classes of the grey antimonial copper found in many parts of this republic (Chili), and in numerous other localities. It is very soft, has a greasy texture, and an intense greenish-grey colour, somewhat inclining to red; its powder is very red, almost as bright as the native protoxide of copper. It is found in the mine *Altar*, belonging to Señor Urmenata, about thirty leagues from Coquimbo, associated with iron pyrites, blende, galena, and yellow sulphide of copper. The analysis was long and troublesome, owing to the well-known difficulties attending the separation of arsenic from antimony, especially when large amounts of sulphur are present. 100 parts gave:

Gold	0·003
Silver	0·075
Copper	36·720
Iron	1·232
Zinc	7·260
Antimony	20·284
Arsenic	3·912
Sulphur	30·350
	99·836

The gold and silver were estimated by cupellation, and afterwards

separated by perfectly pure nitric acid; the iron and zinc by carbonate of baryta, &c.

My friend M. Domeyko, Professor of Chemistry in the University of Santiago, makes the following observations upon some specimens of the same mineral I sent him, which he found to vary considerably in the relative amounts of gold and silver:

"The minerals consist of a mixture of galena, iron pyrites, blende, and grey copper (*cuivre gris*); the matrix is amorphous quartz, very nearly pure. The galena is leafy, composed of leaves of different sizes; the blende is nearly black, very ferruginous, the same that generally accompanies the minerals of gold in Chili, as well as in New Granada, and to which Boussingault has given the name of *Marmatite*. The pyrites is amorphous, at times containing a little sulphide of copper. The gold or silver is not perceptible to the sight in any samples of this mineral.

"I have here the results of some assays, made in my laboratory, of some beautiful specimens sent me by Señor Urmenata and yourself:

1°. Grey copper, perfectly pure, gave:

Silver	0·89 per cent.
Gold	0·01 „

2°. Mixture of grey copper, galena, and pyrites:

Silver	0·15 per cent.
Gold	0·05 „

3°. Mixture of grey copper, galena, blende, and pyrites:

Silver	0·39 per cent.
Gold	0·01 „

In conclusion, I may state that I have seen masses of mineral from the mine containing very large pieces of gold, evidently alloyed to a great extent with silver. One specimen gave no less than 160 ounces troy of gold per ton of mineral.

The gold, however, exists principally in the peculiar mineral, the grey auriferous copper, which occurs in large quantities and of great purity. This mineral, the subject of the above memoir, I believe to be new in mineralogical science.

XXVIII.—*On the Action of Ammonia on Sebacic Ether.*

By Thos. H. Rowney, F.C.S.

ASSISTANT IN THE LABORATORY OF DR. ANDERSON, EDINBURGH.

The following experiments were made to endeavour to ascertain, if possible, whether sebacic acid is a bibasic acid or not. I formerly intended to pursue the subject further, and to investigate the different compounds and products of decomposition, but I am induced to publish my results now, in consequence of having seen in the Chemical Gazette of Oct. 1, 1851, a notice of a paper by M. Bouis, taken from the *Comptes Rendus* of Aug. 11, 1851, from which it appears that M. Bouis has been working in a somewhat similar direction. I had heard some time since from Dr. Hofmann that sebacic acid had been obtained from castor oil, and being then engaged in the examination of the action of ammonia on various oils, I intended to examine its action on castor oil, in order to compare the results obtained in this action, with those obtained by acting with ammonia on the ethyl-compounds of sebacic acid. I was not aware at the time that M. Bouis had examined this action; but as he has done so, and published some account of his results, I have not waited to complete my own experiments, but lay before the Society the results I have obtained by acting on sebacic ether with strong ammonia.

The ether employed for these experiments was obtained by passing a current of dry hydrochloric acid gas into an alcoholic solution of sebacic acid, and then adding water; when the ether had risen to the surface, the acid liquor was syphoned off, and the ether was washed with cold water. Thus obtained, it is an oily liquid of a fragrant odour, insoluble in cold water and very soluble in alcohol. The quantity obtained was too small to allow me to purify it by distillation in order to see its boiling point.

In order to submit it to the action of ammonia, it was dissolved in alcohol, and digested, in a stoppered bottle, with a strong solution of ammonia. After digesting for about a month, a perceptible change took place in the ether; instead of an oily liquid, a bulky and somewhat granular substance made its appearance, from which bubbles of gas were given off. After continued digestion, the evolution of gas ceases, and the substance becomes more granular; and as all action

had ceased, it was filtered and washed with cold water until it was free from ammonia. To obtain it quite pure, it was twice crystallized from alcohol; it then exhibited the following properties.

It is insoluble in cold water, rather soluble in boiling water, slightly soluble in cold alcohol, very soluble in boiling alcohol, and is deposited from this solution in hard, rounded, granular crystals; under the microscope, these are found to be collections of minute needle-shaped crystals. Its solutions are neutral to test paper; it is insoluble in a dilute solution of ammonia; when boiled with a solution of caustic potassa, it gives off ammoniacal fumes, but cold potassa does not act upon it.

The following results were obtained by the analysis of the substance crystallized from alcohol, and dried at 100° C.; the combustions were made with oxide of copper and copper turnings.

FIRST ANALYSIS.

·3449 grammes of substance gave
·7570 „ of carbonic acid, and
·3086 „ of water.

SECOND ANALYSIS.

·3007 grammes of substance gave
·6610 „ of carbonic acid, and
·2649 „ of water.

THIRD ANALYSIS.

·2318 grammes of substance gave
·5102 „ of carbonic acid, and
·2153 „ of water.

FOURTH ANALYSIS.

·2513 grammes of substance, burnt with soda-lime, gave
·5545 „ of platinum salt.

	I.	II.	III.	IV.
Carbon . . .	59·86	59·95	60·02	
Hydrogen . .	9·94	9·78	10·32	
Nitrogen . .	—	—	—	13·85

	Mean.	Calculated.		
Carbon	59·94	20	120	60·00
Hydrogen . . .	10·01	20	20	10·00
Nitrogen . . .	13·85	2	28	14·00
Oxygen	16·20	4	32	16·00
	100·00		200	100·00

These analyses show that the substance was the neutral amide, as will be seen on comparing the numbers obtained by analysis with those calculated.

The ammoniacal mother-liquor and washings were evaporated on a water-bath to a small bulk, and hydrochloric acid was added to it; a copious precipitate was obtained, which was filtered and washed with cold water. It was then dissolved in a dilute solution of ammonia, and filtered to separate it from a small quantity of the sebamide—reprecipitated by hydrochloric acid—filtered and washed until quite free from hydrochlorc acid—and then crystallized from water. It is deposited from its aqueous solution in rounded grains very similar in appearance to sebamide. It is very soluble in alcohol, and also in boiling water; its solution has an acid reaction.

Analysis gave the following results:—

FIRST ANALYSIS.

·2832 grammes of substance gave
·6190 „ of carbonic acid, and
·2418 „ of water.

SECOND ANALYSIS.

·2655 grammes of substance gave
·5810 „ of carbonic acid, and
·2293 „ of water.

THIRD ANALYSIS.

·2167 grammes of substance, burnt with soda-lime, gave
·2315 platinum salt.

	I.	II.	III.
Carbon . .	59·61	59·68	„
Hydrogen . .	9·48	9·59	„
Nitrogen . .	„	„	6·70

	Mean.	Calculated.		
Carbon	59·64	20	120	59·70
Hydrogen . . .	9·54	19	19	9·45
Nitrogen . . .	6·70	1	14	6·96
Oxygen . . .	24·12	6	48	23·89
	100·00		201	100·00

These numbers agree closely with those calculated for the acid amide.

Sebamic acid when dry is very similar in appearance to sebamide, but differs from it in being very soluble in a dilute solution of ammonia; it gives off ammoniacal fumes when boiled with caustic potassa. Its ammoniacal solution gives a precipitate with nitrate of silver soluble in nitric acid, and in excess of ammonia; it also gives a precipitate with acetate of lead but does not precipitate the alkaline earths. Having but little of this substance, I have not been able to examine any of its salts.

From the results of these analyses, I conclude that sebacic acid ought to be considered as a bibasic acid, its formula being $C_{20}H_{16}O_6 . 2HO$, and that the ether obtained in the manner I have described, is in reality a mixture of the acid and neutral ethers. If this be the case, the action of ammonia upon them may be readily explained. In the formation of the neutral amide, we have:

$$C_{20}H_{16}O_6 . 2C_4H_5O + 2NH_3 = C_{20}H_{20}O_4N_2 + 2C_4H_5O,HO,$$

and in the acid amide we have

$$C_{20}H_{16}O_6 . \begin{matrix} C_4H_5O \\ HO \end{matrix} + NH_3 = C_{20}H_{18}O_5N.HO + C_4H_5O,HO$$

leaving in the acid one atom of hydrogen capable of being replaced by bases.

This action of ammonia I found to be constant, as in three separate preparations, sebamide and sebamic acid were always formed.

These exeripments were made in the laboratory of Dr. T. Anderson, of Edinburgh, whom I have to thank for the use of his laboratory and for advice during the progress of this investigation.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 3, 1851.

The President in the Chair.

George Gladstone, Esq., was duly elected a Fellow of the Society.

The following presents were announced:

"On a New Source for obtaining Capric Acid, and Remarks on some of its Salts, by Thomas H. Rowney:" by the Author.

"A Specimen of Capric Acid," by the same.

"The Ceylon Times, of Friday, September 12, 1851:" by the Editor.

"Transactions of the Royal Society of Edinburgh, Vol. XX., Part 2, for the Session 1850—51:" by the Society.

"Proceedings of the Royal Society of Edinburgh, Vol. III., Nos. 40, 41, and the Index to Vol. II.:" by the Society.

"Experimental Researches on the Food of Animals, and the Fattening of Cattle, with Remarks on the Food of Man, by Robert Dundas Thomson, M.D.:" by the Author.

"The Pharmaceutical Journal, Nos. 2, 3, 4, Vol. X.:" by the Editor.

"Proceedings of the Liverpool Literary and Philosophical Society, No. 6:" by the Society.

"The Eighteenth Annual Report of the Royal Cornwall Polytechnic Society, 1850:" by the Society.

"Proceedings of the American Philosophical Society, January—July, 1851."

"An Account of an Apparatus for producing attrition between the surfaces of Siliceous Stones in Vacuo, or in Gaseous Media; and for determining whether the consequent odour and coruscations are due to Ozonification, by Dr. Hare:" by the Author.

"The Chemical Record and Drug Price Current, Nos. 2, 4, 5, 6, 7, 10, 12:" by the Editor.

"The Quarterly Journal of the Geological Society, Vol. VII. No. 27:" by the Society.

"The Journal of the Franklin Institute, Vol. XXI. No. 6, and Vol. XXII, No. 1."

"Memorias de la Real Academia de Ciencias de Madrid, Tomo I. Partie 1."

"Resumen de las actas de la Academia Real de Ciencias de Madrid, 1849—50:" by the Academy.

"Abhandlungen der Mathematisch-Physikalischen Klasse der Königlich Bayerischen Akademie der Wissenschaften. Sechsten Bandes, Erste Abtheilung:" by the Academy.

"Schilderung der Naturverhältnisse in Süd-Abissinien, von Dr. J. R. Roth:" by the Author.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften, Erster und Zweiter Band."

"Tafeln zu den Denkschriften der Kaiserlichen Akademie der Wissenschaften."

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mai—November:" by the Academy.

The following papers were read:

1. "Observations on the Phenomena of Animal Phosphorescence:" by Thornton J. Herapath.

2. "Analysis of a Mineral containing Gold, from the Province of Coquimbo, Chili:" by F. Field.

3. "Description of Lapis Lazuli, found in large quantities in the Cordilleras of the Andes:" by F. Field.

4. "On the Spontaneous Decomposition of Gun-Cotton, and its Congeners: by J. H. Gladstone, Ph.D.

November 17, 1851.

PROFESSOR MILLER, Vice-President in the Chair.

James B. Barnes, Esq., Richard Law Brunton, Esq., Thomas Beesley, Esq., and William H. Stone, Esq., were elected Fellows of the Society.

The following presents were announced:

To the Library.

"Silliman's American Journal of Science and Art, Vol. XII. No. 35:" by the Editors.

"On Agricultural Chemistry, especially in relation to the Mineral Theory of Baron Liebig, by J. B. Lawes and Dr. J. H. Gilbert:" by the Authors.

"Some Observations on the Chemical Composition and Agricultural Value of the Fossil Bones and Pseudo-Coprolites of the Crag, by Thornton J. Herapath:" by the Author.

"Quarterly Journal of the Geological Society, Vol. VII. No. 28:" by the Society.

"Journal of the Franklin Institute, Vol. XXII. No. 3:" by the Institute.

"Literary Gazette, No. 1817:" by the Editor.

To the Museum.

BY MESSRS. KURZ AND SCHMERSAHL.

Four specimens of ultramarine.

BY THE UNITED STATES' COMMISSIONERS.

(PREPARED BY MESSRS. POWERS AND WIGHTMAN.)

Hydroferrocyanate of quinine; citrate of quinine; arseniate of quinine; hydriodate of quinine; valerianate of quinine; acetate of quinine; morphine; cinchonine; valerianate of morphine; sulphate of morphine; narcotine; strychnine, in powder; strychnine, finely-crystallised; nitrate of strychnine; piperine; cubebine; sulphate of brucine; tannin; picrotoxine; santonin; menispermine; molybdic acid; uranic oxide; bromide of potassium; tannate of iron; iodide of sulphur.

BY MESSRS. DINNEFORD AND CO.

Chromate of magnesia; sulphate of magnesia and copper; carbonate of magnesia and potash; nitrate of magnesia; monocarbonate of magnesia, tri-hydrated; monocarbonate of magnesia, penta-hydrated; benzoate of magnesia; oxalate of magnesia; sulphate of magnesia and iron; sulphate of magnesia and soda; sulphate of magnesia; borate of magnesia; solution of bicarbonate of magnesia.

BY MR. RIDGWAY, AGENT FOR BRITISH GUIANA.

Kasareep; laurel-oil; milk from the cow-tree; active principle of capsicums extracted by vinegar; active principle of capsicums extracted by olive-oil; saline ash from lichens; balsam of copaiba; crab-oil; gum-resin from the locust-tree; starch from buck-yam; arrow-root; starch from sweet cassava; starch from bitter cassava; starch from plantain.

BY MR. FRANCIS M. JENNINGS.

Gum from inorganic substances; sugar from potato-starch; oxalic acid from potato-starch; acetic acid from potato-starch; wax from wheat-starch; pure potato-starch; solution of gum-substitute.

BY MR. WENZEL BATKA, OF PRAGUE.

Oxide of nickel; sulphide of cadmium; succinic acid; tungstic acid; carbonate of lithia; selenium from sulphur; tungsten; tungsten-blue; creosote from wood-tar.

BY THE AUSTRIAN COMMISSIONERS.

Laiocom; white lead; dextrin; albumen; mercury from Idria; ground cinnabar from Idria; gumi surrogat; sulphide of mercury; a natural alloy of lead and antimony for printers' types; lead from Bleiberg, Carinthia, said to be free from silver; cobalt-ore; spongy nickel; white iron; spathic iron; antimony; sulphide of antimony; quicksilver-ore from Idria; beetroot-sugar; raw iron; slags from iron.

BY MESSRS. PONTIFEX AND WOOD.

Tartaric acid; citric acid; sulphate of copper; Rochelle salt.

BY MESSRS. SPENCE AND DIXON.

Crystallised alum.

BY MR. GEORGE WHIPPLE.

Two specimens of deposit from oil of bitter almonds.

The following papers were read:

1. "On the Action of Arsenious Acid upon Albumen:" by John B. Edwards.
2. "On the Action of Ammonia on Sebacic Ether:" by T. H. Rowney.

December 1, 1851.

The President in the Chair.

The following presents were announced:

To the Library.

"Literary Gazette, No. 1820:" by the Editor.

"Taylor's Calendar of the Meetings of the Scientific Bodies of London, for 1851—2:" by the Publisher.

To the Museum.

BY THE FRENCH COMMISSIONERS.

Bromate of potassa; anhydrous sulphate of soda; crystallised sulphate of soda; pure alumina; salicin; phosphate of lime for enamels; bromide of potassium; chloride of potassium; chloride of strontium; iodide of lead; albumen from blood; sulphate of soda; a fine crystal of alum; iodide of potassium; iodide of mercury; nitrate of strontia; spongy iron.

BY MR. LLOYD BULLOCK.

Caffeine; urea; uric acid; hippuric acid; allantoine; creatine; creatinine.

BY MR. F. C. HILLS, OF DEPTFORD.

Remarkably fine crystals of nitrate of potash.

BY MR. MOSES HAIM PICCIOTTO.

Gum arabic; the same purified by sulphurous acid; ultramarine; mannite.

BY MESSRS. HOWARD AND KENT.

Pure carbonate of soda; biborate of soda; ammonio-chloride of iron; citric acid; sulphate of iron; tartrate of potash; iodide of potassium; nitrate of potash.

BY THE PATENT BITUMINOUS SHALE COMPANY.

Three specimens of the products derived from the distillation of shale.

BY MESSRS. MORSON AND SON.

Hydriodate of morphine; gallic acid; pure strychnine; furfuramide; sulphate of morphine; pure tannin: sulphate of strychnine; soluble cream of tartar.

December 15, 1851.

The President in the Chair.

George Henry Bachhoffner, Ph.D., R. Oxland, Esq., Edward Riley, Esq., Lionel S. Beale, Esq., Thomas Morson, Jun., Esq., and Edward Hunt, Esq., were duly elected Fellows of the Society.

The following donations were announced:

To the Library.

"The Introductory Lectures delivered at the Museum of Practical Geology, by Sir H. De la Beche, Dr. Lyon Playfair, Mr. Edward Forbes and Mr. Robert Hunt:" by the Authors.

"The Literary Gazette, No. 1821:" by the Editor.

"Physiological Researches, by Sir Benjamin C. Brodie, Bart.:" by B. C. Brodie, Esq.

To the Museum.

BY MESSRS. SAVORY AND MOORE.

Valerianic acid; valerianate of silver; valerianate of ethyl; valerianate of copper; valerianate of potash; valerianate of strontia; valerianate of cadmium; valerianate of nickel; valerianate of manganese; valerianate of bismuth; valerianate of magnesia; valerianate of ammonia; valerianate of zinc; valerianate of soda; valerianate of suboxide of mercury; valerianate of copper; valerianate of alumina; valerianate of sesquioxide of iron; valerianate of lime; valerianate of chromium.

BY MR. DAVENPORT.

Iodide of lead; nitrate of potassa; benzoic acid; collodion; neutral sulphate of quinine; gallic acid; iodide of potassium; hyposulphite of soda; ammonio-citrate of sesquioxide of iron; ammonio-citrate of protoxide of iron; citrate of iron and quinine; citrate of sesquioxide of iron; citrate of protoxide of iron.

BY MESSRS. HOWARD AND KENT.

Crystallised calomel; amorphous calomel; hydro-calomel; white precipitate; black sulphide of mercury; corrosive sublimate; red precipitate; oxide of mercury; binoxide of mercury; sulphate of mercury.

BY B. C. BRODIE, ESQ.

Specimen of Chinese wax.

The reading of Dr. Frankland's Report "On the Manufacture of Water Gas," was concluded.

Dr. Williamson gave a preliminary announcement of the discovery, by Mr. Duffy, of an isomeric transformation of certain fats. The true melting point of stearin is about 51° C., and that of palmitin 46° C.; but at these temperatures they gradually solidify, and in a modified state, the melting points being then about 62° for stearin, and 61° for palmitin.

Dr. Gladstone presented a specimen of subiodide of phosphorus to the Society. This is a solid body of a red colour, and undecomposable by water; it is produced by bringing two parts of iodine and one part of phosphorus into combination, or by reducing the scarlet teriodide by excess of phosphorus. Synthetical experiments tended to indicate the composition $P_2 I$, but analytical results always showed a much larger amount of phosphorus: however, the substance was not obtained uniform in composition.

A paper was read "On the Oxidation of Chinese Wax:" by Neville Story Maskelyne, Esq.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

Dr. Lawrence Holker Potts, one of the original Members of this Society, was born in London, on the 12th of April, 1789. His father was a medical practitioner in Pall Mall. At an early age, he was for a short time at Westminster School, from which he was removed to Northamptonshire, where he finished his education. Being designed for the medical profession, he was apprenticed to a gentleman in Warwick, after which he became a house pupil to Sir Benjamin Brodie, for two years. In 1812, he passed his examination as a surgeon, and was appointed to the Royal Devon and Cornwall Militia. On this regiment being disbanded, in 1814, he settled at Truro, pursuing, as his leisure time would admit, his favourite studies in chemistry and mechanics. With the mineralogy of Cornwall he was well acquainted, and possessed a fine collection of cabinet specimens, some of the best of which were lately presented to Prince Albert, for the Prince of Wales. In 1818, Dr. Potts, in conjunction with other gentlemen, originated the Royal Institution of Cornwall, and to its advancement he devoted as much of his time as could be snatched from his professional engagements. In 1825, he took his degree of Doctor of Medicine, and in 1828 was appointed superintendent and physician to the Cornwall Lunatic Asylum. From this position he removed to London, and having taken a lease of Vanburgh Castle, Blackheath, opened it as an establishment for the treatment of spinal diseases in young ladies. Among his numerous manuscripts is a work nearly complete on spinal complaints. It was shortly after this period, that he made his great discovery for sinking tubes, cylinders, or coffer-dams, by atmospheric pressure; and the time and attention required to bring this invention into practice, obliged him, at a great pecuniary sacrifice, to relinquish his previous undertaking. This invention, although highly approved by the Trinity Board, the Lords of the Admiralty, and other highly influential parties, required a long and impoverishing struggle to

bring it into extensive operation, and he just survived to see the likelihood of its important application under the able management of Messrs. Fox and Henderson, when he expired, after a long and painful illness, on the 23rd of March, 1850.

The beautiful adaptation of atmospheric pressure, which forms the subject of Dr. Potts's invention, was first tried by him, on a large scale, on the Goodwin Sands, on the 16th of July, 1845, when an iron tube, 2 feet 6 inches in diameter, was driven into the sand to a depth of 22 feet in two or three hours; the greatest depth attained has been 70 feet. The method of operating is to place the tube, or cylinder, in a perfectly vertical position, resting on the bed of the river, or sea bottom. By means of a cap and an elastic tube, this is connected with an exhausted receiver, and on the communication between the two being opened, the pressure of the atmosphere on the surface of the water, produces such a rush to fill the vacuity in the interior, that it carries on a constant excavation under the lower edge of the tube, which rapidly sinks by its own weight, aided by that of the surrounding air; this operation is repeated as often as necessary, fresh lengths of tube being added as required, until a rocky or firm foundation is reached; the contents are then pumped out, and the interior filled with concrete, or, when of sufficient magnitude, with solid brickwork or masonry. If any impediment is met with, the apparatus can be readily converted into a diving-bell, by simply reversing the action of the air, and the men can work dry within the cylinder, until such obstruction has been removed. By this means, beacons have been erected by the Trinity Board on the Margate, the Girdler, the Shingly, the Buxhey, and other sands, lying at the mouth of the Thames; and also several of the railway bridges, as at Huntingdon and Peterborough, on the Great Northern Railway; the bridge over the Thames, at Windsor; the new bridge over the Medway, at Rochester; and one over the Shannon, the cylinders of which are 10 feet in diameter, and were carried through several feet of yellow clay. In Cornwall, a shaft has been sunk at Wheal Ramoth Mine, under the sea, by this means.

Dr. Potts was an ardent lover of science, and his devotedness to its cause was constant and persevering.

James Thomson, Esq., F.R.S., was born at Blackburn, on the 6th of February, 1779. His family were nearly connected with that of the late Sir Robert Peel. At the early age of fifteen he went to pursue his studies at Glasgow. There he entered into relations of

confidential friendship with Gregory Watt (son of the immortal improver of the steam-engine), after whose early death he remained on terms of intimacy with James Watt himself, and Thomas Campbell, author of the "Pleasures of Hope," whose distinguished poetical genius he early felt and appreciated.

After remaining at college a year, he entered the mercantile house of Joseph Peel and Co., in London. In this capital he resided for six years, associating with the most remarkable literary and scientific men of the age. Sir Humphrey Davy, Wollaston, and Porson, were amongst his intimate friends. His knowledge of the then little cultivated science of chemistry attracted the notice of his employers, who, thinking it might be rendered more available in the manufactories of Lancashire than in a London counting-house, removed him to their establishment near Accrington. Here he remained nine years, having in the meantime married Cecilia, eldest daughter of the Rev. Thomas Starkie, Vicar of Blackburn.

In the year 1811, he established himself at Primrose, near Clitheroe, where he pursued the occupation of calico-printing for nearly forty years.

Notwithstanding the claims and difficulties of an arduous business, he devoted much time to the cultivation of general science and literature. He was besides a generous patron of the arts, and a liberal contributor to all public institutions. His power as a writer is well known to all his acquaintances, and it is much to be regretted that he has left behind him no further specimens of his talent for composition than are comprised in a few short though masterly pamphlets. His scientific knowledge and highly cultivated taste, combined with the great energy and enterprise of his character, placed him in the very foremost rank amongst the distinguished and philosophical manufacturers of his time; and in the neighbourhood where he resided, and to the prosperity of which he may be considered as having so largely contributed, his name will long be remembered with gratitude as a friend and benefactor.

In Davy's Chemical and Philosophical Researches on Nitrous Oxide, published in 1800, he gives some observations received by letter, dated October 28th, 1799, from his "ingenious friend Mr. James Thomson," relating to the composition of nitrous acid, who from experiments therein alluded to, considers that "nitrous acid is nothing more than nitric acid holding nitrous gas in solution." The accuracy of these views is not a question for consideration now, but it will fully illustrate the originality of Mr. Thomson's talents, and the estimation in which he was held by so eminent a philosopher as

Sir Humphrey Davy. From the same work we learn that Mr. Thomson was one of the first, in association with Southey, Coleridge, and other intimate friends of Davy's, to inhale the nitrous oxide gas, an account of the effects of which are given in a letter contained in the appendix to this work. In "Nicholson's Journal," for 1809, p. 174, we find a paper "On the Analysis of Sulphate of Barytes," by Mr. James Thomson, which contains analyses, not only of the sulphate, but also of the carbonate and nitrate of barytes, as also of sulphate of lime. By comparing his results with those now generally considered as accurate, it will be found that very little difference exists. About the year 1822, Mr. Thomson commenced his investigation of the mummy-cloth of Egypt, which had up to that period been considered as consisting of cotton. After various experiments to determine this point, he states: "It occurred to me that the supposed unfitness of cotton lint, compared with linen, for dressing wounds, had been accounted for by the different form of their fibres, the one being sharp and angular, and the other round and smooth; and, in fact, I found in the twelfth volume of the Phil. Trans. for the year 1678, this structure ascribed to them by that early microscopic observer, Mr. Leuwenhoek. *It seemed to me, therefore, that the most simple mode of distinguishing between cotton and linen would be to subject the fibres to examination under a powerful microscope.* Not being possessed of such an instrument, or accustomed to its management, my friend, Mr. Children, undertook, through Sir Everard Home, to solicit the assistance of Mr. Bauer. I transmitted to him various pieces of cotton and linen, both manufactured and in their raw state, as well as fibres of unravelled mummy-cloth, and received from him a letter dated September 16th, 1822, in which he pronounced every specimen of mummy-cloth subjected to his examination to be linen." We have been more particular in giving these details, as a claim of priority to this discovery has been set up by other parties. Mr. Thomson was still occupied, during the few leisure hours he could command from the engagements of his extensive establishment at Primrose and his infirm health would admit, in a long-pending discussion on this subject with some Italian philosophers, up to the time of his decease. These results have been as yet but partly published, the manuscripts and drawings for the completion of the subject being in the hands of his son-in-law, Dr. Braun.

NOTICES

OF

PAPERS CONTAINED IN

British and Foreign Journals.

On the Constitution of Salts.

By Alexander W. Williamson.*

There is strong reason for believing that all questions concerning the chemical constitution of matter, will be most tangible when considered from the point of view of the constitution of salts, which are the groups whose arrangement and transformations are most susceptible of being ascertained experimentally. The elementary bodies themselves have been now shown† to obey a certain force of combination between their particles, analogous, though generally inferior, to that which holds together the constituents of a salt; and any general conclusions which may be established for salts, will therefore extend to them. Now, to have clear and connected notions of any order of phenomena, it is necessary to be able to judge of the various cases belonging to it from the same point of view, or, in other words, to have a uniform standard of comparison. Thus if the value of mechanical forces had to be compared, it would evidently not do to measure the one in pounds and the other in kilogrammes, unless the relative value of these units were known, *i. e.* unless the statement made in the one could be reduced to its equivalent in the other. Such unity has as yet been but little attended to by the majority of chemists; and the different branches of the science remaining disconnected, their efforts have been directed to establish details rather than general laws. Thanks to the numerous facts which have been thus established, it is now possible, and even necessary, to do something more. The researches of MM. Laurent and Gerhardt have been mainly directed to this point, and it is well known how fruitful their conclusions have already proved. The following remarks have an intimate connection with those conclusions, and will hardly be intelligible without a knowledge of them.

* Chem. Gaz. 1851) the entire paper).

† See Mr. Brodie's research "On the Condition of certain Elements at the moment of Chemical Change."

We are all agreed that chemistry is concerned with the material process of the transformations and changes which matter undergoes, and that the study of the properties of matter in themselves, as long as they undergo no change, belongs to physics. The chemical formulæ, by which we describe more briefly than by words the transformations supposed or known to take place, have as yet answered that purpose very imperfectly, and have presented great irregularity of method; for, although generally denoting a certain arrangement of atoms, or at least certain differences of arrangement, they are sometimes used to describe the origin of a compound or its decompositions, without forming any other representation of its actual constitution than what may be contained in such a statement. M. Gerhardt has, in a recent memoir published conjointly with M. Chancel, given considerable development to this latter method; and his so-called synoptic formulæ will, I think, be found very suggestive and useful expressions. But formulæ may be used in an entirely different, and yet perfectly definite manner, and the use of two distinct points of view will perhaps not be unserviceable. They may be used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system; and decompositions may be actually effected between them by the exchange of a molecule in one group for a molecule in another. Gerhardt's formula for sulphate of soda (if he extends his principles to inorganic chemistry) would be sulphuric acid *plus* soda *minus* water. This, no doubt, gives a possible origin of the salt, but by no means a possible decomposition; in other instances, the inverse would be the case. But the term sulphate of soda does not mean a body formed in any one particular way; it is equally applicable to the product of the action of sulphuric acid on chloride of sodium, or on carbonate of soda, or even to the product of the action of soda on sulphate of iron. The written name should be made to represent what we conceive a compound *to be*, and should be such that it might be formed by any one of the various processes by which the compound may be prepared. Sulphate of soda is a physical term, and corresponds to purely physical properties; for the substance described by it does not by itself undergo any change, but only when acted upon by certain foreign substances under suitable circumstances.

When we study a molecule by itself, we study it physically; chemistry considers the *change* effected by its reaction upon another molecule, and has to describe the process by which that change is effected. A chemical decomposition should therefore be represented by the juxtaposition of the formulæ of the reacting substances, and by effecting in these formulæ the change which takes place in the mixture.

The adoption of such a method will of course necessitate the adoption of types, from which, by the replacement of certain ele-

ments or molecules, we can deduce the constitution of more and more complex groups. I believe that throughout inorganic chemistry, and for the best known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\overset{H}{H}O$. In many cases a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids, &c.

I will here give a few examples of the application of this universal type to the formulæ of common substances. The experiments of M. Chancel, agreeing in result with my own, have clearly proved that the numerous family designated as hydrated oxides are not formed by the juxtaposition of an atom of water with an atom of metallic oxide, *e. g.* $K_2O + H_2O$, but that the equivalent of the molecule is half of that quantity, namely $\overset{H}{K}O$; they are not compounds of water, but products of substitution in water. This fact is as applicable to the compound as to the simple radicals; and alcohols, which are truly hydrated oxides, must be considered as products of substitution of the compound radicals, methyl, CH_3; ethyl, C_2H_5; amyl, C_5H_{11}; capryl, C_8H_{17} (Bouis), &c. for half the hydrogen of water, $\overset{H}{CH_3}O$, $\overset{H}{C_2H_5}O$, &c. The anhydrous oxides of metals have both atoms of hydrogen replaced by the metal, as $\overset{K}{K}O$, in the same way as common ether and its homologues have ethyl in place of both the atoms of hydrogen.

In extending this mode of notation to salts and compound ethers, we must of course keep carefully in view the capacity of saturation of their acids, writing the monobasic acids, such as hydrochloric, nitric, acetic, &c., at half their usual equivalents, ClH, NO_3H, $C_2H_4O_2$, but retaining the customary atomic weights of the bibasic acids, as sulphuric, carbonic, oxalic, &c.

As alcohol is truly an acid in its reaction, we must of course consider the potassium-alcohol, $\overset{C_2H_5}{K}O$, as its salt, though alkaline in its reactions. We only need to replace 2 atoms of hydrogen in the radical of this salt by oxygen, to have a compound of which the saline character is acknowledged, viz., acetate of potash, $\overset{(C_2H_3O)}{K}O$. The most simple manner of representing the rational constitution of this compound is to state that it contains, in lieu of the ethyl of the former salt, an oxygen-ethyl, C_2H_3O, which we may term *othyl*. If the 2 atoms of hydrogen in water were replaced by this othyl, we should have anhydrous acetic acid, $\overset{(C_2H_3O)}{(C_2H_3O)}O$. In fact, the so-called

anhydrous acids are nothing else than the *ethers* of the hydrated acids. Again, by replacing the potassium in the ethylate, $\frac{C_2 H_5}{K} O$, by its equivalent of cyanogen (which may be effected by the action of iodide of cyanogen), we obtain a compound of the composition $\frac{C_2 H_5}{(NC)} O$, that is, cyanic ether. It is well known, from Wurtz's elegant researches, that by acting upon this body by hydrate of potash, we obtain carbonate of potash and ethylamine; that is, in the place of carbonic oxide in the cyanate, we get hydrogen, and reciprocally with the hydrate. Now can this exchange be represented more simply than by stating the fact, that, in the following diagram, the hydrogen of the 2 atoms of hydrate of potash changes places with the carbonic oxide of the cyanate?—

$$\begin{matrix} & K_2 & & & K^2 & \\ & & O_2 & & & O_2 \\ & (H_2) & & & (CO) & \\ C_2 H_5 & & = & C_2 H_5 & & \\ & (CO) & & & (H_2) & \\ N & & & N & & \end{matrix}$$

1 atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, holds together the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\frac{(CO)}{K_2} O_2$, carbonate of potash.

If we knew how to form the compound COCl, *i.e.*, phosgene, with half as much chlorine, it would be easy, by its reaction upon our ethylate of potassium, to prepare oxalic ether (and chloride of potassium). Oxalic ether is therefore alcohol in which the basic hydrogen is replaced by carbonic oxide with twice the equivalent that it possesses in the carbonates; and the best evidence of the truth of this view, is afforded by M. Dumas' elegant reaction of ammonia upon the ether, forming the compound of amidogen with carbonic oxide (oxamide), and replacing the carbonic oxide by hydrogen, *reproducing alcohol*:—

$$\left.\begin{matrix} 2\,C_2 H_5 & & \\ & O_2 & \\ (CO)_2 & & \\ H_2 & H_4\, N_2 & \end{matrix}\right\} = 2\left(\begin{matrix} C_2 H_5 & & \\ & O & \\ & H & \\ (CO)_2 & H_4\, N_2 & \end{matrix}\right).$$

Sulphurous acid is another radical capable of replacing hydrogen; and the sulphates are thus reduced to our type, being bibasic for the same reason as the carbonates. We have thus for sulphuric acid, $\frac{SO_2}{H_2} O_2$; acid sulphate of potash, $\frac{SO_2}{HK} O_2$; neutral sulphate, $\frac{SO_2}{K_2} O_2$, &c.

There are various reactions, both of formation and decomposition, of sulphates, which bear out this view; for instance, chlorosulphuric acid, SO_2Cl_2, in contact with 2 atoms of water, at once replaces half the hydrogen in both by SO_2, forming 2(ClH) and $\frac{SO_2}{H_2}O_2$. And again, the difference of the action of zinc upon sulphuric acid according to the concentration, evolving at one time hydrogen, at another sulphurous acid, affords evidence that the sulphurous acid is contained in a manner similar to the hydrogen.

Nitric acid presents, according to the usual view of its constitution, a singular difference between its behaviour to organic and to inorganic compounds; but this difference is owing merely to the error of that view. We are taught that nitric acid combines directly with mineral bases; but when reacting upon hydrogen compounds, it has a powerful tendency to replace hydrogen by hyponitric acid. Now if hydrogen, in organic compounds without number, be replaceable by hyponitric acid, why should not also the hydrogen in hydrate of potash be so replaceable? The product of that substitution would be no very improbable body, only common nitrate of potash, $\frac{(NO_2)}{K}O$.

One more example, and I have done. Chlorine is well known to react upon hydrogen-compounds by replacing hydrogen by chlorine, with formation of hydrochloric acid. So it is also when it reacts upon water in presence of bases, $\frac{Cl}{H}O$ (hydrated hypochlorous acid), and ClH being formed. In like manner we have, for the series of oxygen-acids of this radical, the formulæ $\frac{(ClO)}{H}O$, chlorous acid; $\frac{(ClO_2)}{H}O$, chloric acid; $\frac{(ClO_3)}{H}O$, perchloric acid.

In order to accomplish what I above alluded to as a desideratum for the explanation of chemical reactions, namely, effecting between the formulæ of the reagents the interchange supposed to take place in the mixture, I make use of a kind of movable diagram, in which the symbols of those atoms which have to change places, are placed upon the extremities of a piece of card, so fixed by a pivot to the board, that by turning round 180°, it reverses the positions of the exchanging atoms.*

I would not have brought before the public considerations so purely theoretical as the above, had I not found the conclusions of considerable practical utility in the study of reactions.

In the theory of types, we owe to M. Dumas an idea which has already been the vehicle of many an important discovery in science, and which is undoubtedly destined to receive still more general application.

* See p. 231.

To prevent misunderstandings, it may be as well to state, that the radicals which I have here so freely used, are not supposed to be in their compounds absolutely the same as in the free state. The same remark applies with equal force to metallic bodies, which on entering into combination, give off a certain amount of heat, and thus assume different properties. To say that metallic zinc is contained in its sulphate, is an expression authorized by usage, but is only strictly true by abstraction from most of the properties of the metal. The material atom, which under certain circumstances possesses the properties which we describe by the word "zinc," is no doubt contained in the sulphate, but with different properties, and in the chloride with properties different from either; so also of the compound radicals.

It is to be hoped that we may soon be able to give an account of the nature of the processes by which these changes of properties are effected; but that task can only be entered upon when we have obtained exact determinations of the relative momentum of atoms in various compounds, the proportion of which to their masses determines their physical and chemical properties.

On a Class of Ammoniacal Compounds of Cobalt.

By Frederic Claudet.*

When ammonia is added in excess to a solution of protochloride of cobalt mixed with four times its weight of chloride of ammonium, the solution becomes of a dark brown colour without any appearance of a precipitate. In this state, the solution rapidly absorbs oxygen from the air; and on frequently agitating a bottle half-filled with it, removing the stopper from time to time to renew the air, the absorption is much facilitated, and is complete in the space of three or four days, the colour of the liquid changing at the same time from dark brown to an intense violet-red. If the air be replaced in this experiment by pure oxygen gas, the oxidation is still more rapid, and may be completed (if the quantity of solution be not too large) without requiring the removal of the stopper. By boiling this oxidized ammoniacal solution, strongly acidified with hydrochloric acid, a heavy crimson powder is deposited. A slight effervescence takes place at the same time, due to the evolution of a certain quantity of oxygen, and the liquid becomes nearly colourless, owing to the precipitation of the whole of the cobalt in the form of the new compound. The liquid when cold is drawn off from the red powder,

* Phil. Mag. [4] II, 253

which is washed several times by decantation with distilled water, thrown on a filter, and allowed to dry in a warm chamber. The precipitated powder thus obtained is nearly pure. Before examination it is, however, necessary that it should be crystallized. The powder for this purpose is dissolved in boiling water to which a few drops of hydrochloric acid have been added; and on cooling, the salt is deposited in the form of regular octohedrons, small, sparkling, and of a ruby-red colour, very much resembling small crystals of chrome-alum.

This salt, which is an intense colouring matter, is sparingly soluble in cold water, 1 part requiring at 60° F. 244 parts of water; it is soluble to a much larger extent in water at the boiling-point, to which it imparts a very deep red colour; it is however slightly decomposed, and altogether so on boiling the solution; but this may be prevented by keeping the solution slightly acid with hydrochloric acid.

Hydrochloric acid, and saturated solutions of chloride of ammonium and sodium, completely precipitate the new salt from its solution; alcohol acts in the same way. The salt is not decomposed by boiling hydrochloric acid. Sulphuric acid evolves hydrochloric acid, a corresponding sulphuric salt being formed; the reaction, however, is not complete, for at the end of the operation, chlorine comes off from some decomposition. Nitric acid partially transforms the salt into the nitrate of the base. Potash and soda decompose the solution of the salt, a hydrated peroxide of cobalt being thrown down and ammonia evolved in considerable quantity. Hydrate of baryta decomposes the salt in the same way with the aid of heat, but not in the cold. Carbonate of potash or soda has no effect. Yellow prussiate of potash gives with a solution of the salt a dirty brown precipitate, red prussiate none; but on standing, bright yellow needles crystallize from the solution.

Sulphuretted hydrogen precipitates the whole of the cobalt as a bisulphide of that metal, ammonia being liberated at the same time. The analysis of three different preparations of this sulphide gave—

	Calculated.		Found.		
			I.	II.	III.
Cobalt . .	29·5	47·96	48·9	49·5	48·2
Sulphur . .	32·0	52·04	51·1	50·5	51·8
	61·5	100·00			

On boiling a solution of the new salt, it is decomposed into ammonia, which escapes, and a superior hydrated oxide of cobalt, containing a certain amount of a nitride of cobalt which is precipitated, nothing but chloride of ammonium remaining in solution.

The composition of the precipitated oxide of cobalt appears to be Co_3O_4+3HO.

Dried in the air, the salt contains no water of crystallization, neither does it contain oxygen. When heated to low redness in a glass tube, a large quantity of ammonia is disengaged, a certain quantity of chloride of ammonium sublimed, and a residue of common protochloride of cobalt remains. In this reaction, no moisture is produced, which would necessarily be formed if any oxygen existed in the compound.

The analysis of this salt was effected in the following manner. The chlorine was estimated from the chloride of silver, obtained on boiling the solution with an excess of nitrate of silver and nitric acid. In the cold, the precipitation by nitrate of silver is not complete. The cobalt was determined by reducing a certain quantity of the substance introduced into a tube with a bulb, by pure hydrogen and heat. The nitrogen was estimated as ammonia, by distilling the salt with caustic soda, receiving the ammonia into hydrochloric acid, and determining the weight of the double chloride of platinum and ammonium. The ammonia was also obtained by heating the salt with soda-lime, according to the method of Will and Varrentrapp. This last process, however, gave less accurate results, a deficiency of about 1 per cent in the nitrogen being found. The hydrogen was determined by combustion of the salt with a mixture of oxide of copper and chromate of lead, and copper turnings.

The number of equivalents of chlorine, cobalt, nitrogen and hydrogen, thus determined, are 3Cl, 2Co, 5N and 16H :—

	Calculated.		Found.		
			I.	II.	III.
3Cl =	106·5	42·35	42·22	42·38	42·25
2Co =	59·0	23·46	23·63	23·50	23·66
5N =	70·0	27·83	27·20	27·79	
16H =	16·0	6·36	6·31	6·34	6·46
	251·5	100·00			

The salt containing a large quantity of chlorine, it might be expected that the volatilization of minute quantities of chloride of copper or chloride of lead in the combustion would give an increase in the results for the hydrogen, one equivalent of the latter making a difference only of 0·37 per cent. The results obtained, however, agree pretty well together; and as they do not differ much from the calculated numbers, it is highly probable that sixteen is the true number of equivalents of hydrogen in the salt; and this view is further confirmed by the manner in which the salt is decomposed by heat. A combustion-tube about two feet long was closed at one end and bent at right angles within about half an inch of the closed end, so as to

form a kind of retort. A certain quantity of the salt was rubbed into a paste with a little water and rolled up into the size of a pea. When quite dry, this was dropped into the tube and made to enter the small retort; mercury was then gently poured into the tube, which was gradually filled and then inverted in a mercurial trough. The mercury descended about a quarter of an inch in the tube, on account of a small quantity of air which remained in that portion containing the salt. The retort part of the tube was now slowly heated by means of a spirit-lamp until the salt was entirely decomposed. The gas produced occupied nearly the whole of the tube, which was two feet in height. On allowing the tube to cool, and introducing a small quantity of hydrochloric acid, the whole of the gas was absorbed, with the exception of a column of about three-quarters of an inch in height, showing that the space above the mercury was entirely composed of ammoniacal gas. Now, the decomposition of this salt into no other gas than ammonia, and no other solid products than chloride of ammonium and protochloride of cobalt, is only compatible with a certain number of atoms of hydrogen, which is sixteen; for—

$$3Cl, 2Co, 5N, 16H = 2CoCl + NH_4Cl + 4NH_3.$$

Had there been one or two equivalents less of hydrogen, one equivalent of ammonia would have been broken up, giving hydrogen and nitrogen not condensed by the hydrochloric acid.

Assuming, then, the above number of atoms to be correct, and applying Berzelius's theory of the copulated compounds, the formula of this salt may be written—

$$3(NH_4Cl) + 2(NH_2Co);$$

that is, a compound of 3 equivalents of chloride of ammonium with 2 equivalents of an ammonia in which 1 atom of hydrogen is replaced by cobalt. In fact the salt has the characters of such conjugate compounds. It has the properties of chloride of ammonium with regard to form and taste; while, on the other hand, the basic properties of the 2 equivalents of ammonia have totally disappeared, the salt being quite neutral to test-paper. This compound is analogous to the remarkable platinum-compounds discovered by Gros and Reiset: but with this difference, that it is a sesqui-conjugated compound, if it may be so called, being composed of 3 equivalents of the salt united with 2 equivalents of the adjunct.

Another way of grouping the atoms of this compound is the following, proposed by Mr. Graham:—

$$Cl_3 \left\{ \begin{matrix} NH_2\ Co_2 \\ NH_3,\ NH_4 \\ NH_3,\ NH_4 \end{matrix} \right.$$

Here $NH_2\ Co_2$ represents an ammonium in which 2 equivalents of

hydrogen are replaced by 2 equivalents of cobalt; while $NH_3\,NH_4$ represents an ammonium in which 1 equivalent of hydrogen is replaced by ammonium itself, as the hydrogen of ammonia is replaced by ethyl, methyl, &c. in Wurtz's and Hofmann's bases. Or

$$Cl\,N\left\{\begin{matrix}H_2\\Co_2\end{matrix}\right. + 2Cl\,N\left\{\begin{matrix}H_3\\NH_4\end{matrix}\right.$$

The compound would then be viewed as a double salt, composed of one equivalent of a chloride of cobalt-ammonium and 2 equivalents of a chloride of ammonium, in which the fourth atom of hydrogen is replaced by ammonium.

This peculiar compound has the property of forming double salts with bichloride of platinum and protochloride of mercury.

Double salt with bichloride of platinum.—On adding a warm solution of the salt to bichloride of platinum in excess, a silky crystalline buff-coloured precipitate falls down, much less soluble than the salt itself; it may therefore be washed with water, thrown on a filter, and dried.

12 grains of this double salt were fused with carbonate of soda, dissolved in hot water and filtered, to separate the platinum and oxide of cobalt. The solution neutralized with nitric acid and precipitated with nitrate of silver, gave 20·11 grs. $AgCl = 4{\cdot}975\ Cl = 41{\cdot}6$ per cent. The filtrate of platinum and oxide of cobalt, after being ignited, was treated with boiling hydrochloric acid, which dissolved out the cobalt, and left 4·05 platinum = 33·75 per cent.

18·59 grains of double salt reduced by hydrogen gave 8·06 mixed metals = 43·35 per cent, giving 9·60 per cent for the cobalt. The double salt is consequently composed of 1 equivalent of the new compound and 2 equivalents of bichloride of platinum.

	Calculated.		Found.
$5Cl$	$=248{\cdot}5$	$42{\cdot}12$	$41{\cdot}60$
$2Pt$	$=256{\cdot}2$	$33{\cdot}43$	$33{\cdot}75$
$2Co$	$= 59$	10	$9{\cdot}60$
$5N$	$= 70$		
$16H$	$= 16$		

the formula of which is—

$$Cl_3\left\{\begin{matrix}NH_2Co_2\\2(NH_3NH_4)\end{matrix}\right. + 2PtCl_2.$$

When this salt is decomposed by heat, treated with nitro-hydrochloric acid, and the excess of acid driven off by heat, the solution crystallizes in large, orange-brown, prismatic tables, no mother-liquor remaining. This salt proves to be a double chloride of platinum and cobalt, the 2 equivalents of bichloride of platinum combining

with 2 equivalents of protochloride of cobalt from the new compound.

Double salt with protochloride of mercury.—Prepared in the same way as the preceding double salt, by adding a warm solution of the cobalt-salt to an excess of protochloride of mercury, a bulky silky precipitate is formed, composed of small red needles. This may be collected on a filter, slightly washed with cold water, and recrystallized from a warm solution, the double salt being tolerably soluble in hot water.

15 grains fused with carbonate of soda in the same way as the double platinum-salt, gave 18·10 grs. Ag Cl=4·477 Cl=29·84 per cent.

14·16 grs. reduced by hydrogen gave 0·10 cobalt=5·65 per cent.

	Calculated.		Found.
9Cl	=319·5	30·00	29·84
6Hg	=600		
2Co	= 59	5·54	5·65
5N	= 70		
16H	= 16		

This double salt contains, therefore, for 1 equivalent of the cobalt compound, 6 equivalents of protochloride of mercury.

$$Cl_3\left\{\begin{matrix}NH_2Co_2\\2(NH_3\,NH_4)\end{matrix}\right. + 6Hg\,Cl.$$

Recently prepared oxide of silver throws down the chlorine from the new ammoniacal compound, a highly alkaline red solution remaining, not having the slightest odour of ammonia. On standing, for a few hours, it decomposes, ammonia is evolved, and hydrated peroxide of cobalt precipitated. The compound in solution represents, before changing, the base of the present class of salts. It is an oxide, of which the composition is the same as that of the chloride already described, with the substitution of 3 equivalents of oxygen for 3 equivalents of chlorine :—

$$\text{Formula of new cobalt base . . . } O_3\left\{\begin{matrix}NH_2Co_2\\NH_3NH_4.\\NH_3NH_4\end{matrix}\right.$$

The study of this and other allied compounds of cobalt which exist, will no doubt greatly extend our views respecting the compound ammonias.

The chlorine of the original chloride may also be eliminated by any silver-salt, an analogous cobalt-salt containing the acid of the silver salt being formed and remaining in solution. In this way, a sulphate, nitrate, oxalate, acetate, and carbonate of the new base have been obtained. From the carbonate, the author has prepared the bromide

and iodide, which have the octohedral form of the chloride, are just as sparingly soluble in water, and of a still darker ruby colour. The bromide was found to contain 61·15 per cent of bromine, the calculated amount being 61·8 per cent.

The insolubility, of this ammoniacal compound of cobalt in boiling hydrochloric acid may be advantageously turned to account in the preparation of chemically pure cobalt, and also in the qualitative examination of substances containing small quantities of cobalt. The pulverized ore, or its oxide to be purified, is dissolved in nitro-hydrochloric acid, diluted with water, and filtered in order to separate any gangue or insoluble residue. Chloride of ammonium is now added in large excess, and the liquid saturated with ammonia; it is then poured into a glass bottle, and oxidated in the way already described in the preparation of the new salts. During the oxidation, a certain quantity of the new compound is deposited, especially when the solutions are rather concentrated, on account of its insolubility in a strong solution of chloride of ammonium. The solution still retains a certain quantity of cobalt-salt; it is therefore boiled with a considerable excess of hydrochloric acid, which causes the total precipitation of the new compound, dissolving at the same time any oxide of iron or other oxides thrown down by the ammonia. When cold, the clear liquid is decanted off, and the deposit well washed with acidulated water and then dried. By heating this compound to low redness, it is decomposed, leaving for residue, protochloride of cobalt slightly decomposed, but absolutely free from any other metal. This may be reduced by hydrogen gas, giving pure metallic cobalt.

By these means, the author has been able to prepare perfectly pure cobalt directly from the grey cobalt-ore of Tunaberg, which is an arsenio-sulphide of cobalt, and also to detect small quantities of cobalt in different samples of oxide of nickel.

The preceding results embody the most definite conclusions of an investigation of the ammoniacal salts of cobalt which Mr. F. Claudet has had in hand for the last two or three years. M. Frémy has also lately announced that he is occupied with an extended inquiry into the same class of compounds, respecting which he has published some important general results.* Dr. A. Genth† appears also to have formed several of the salts of the new base above described, but his analytical results differ entirely from those given in the present paper.

* Compt. Rend., April 7, 1851, and May 26, 1851.
† Chem. Gaz. 1851, 286.

On the Composition of Ricinolamide and the Production of Caprylic Alcohol.

By J. Bouis.*

When castor-oil is placed in contact with ammoniacal alcohol, or simply with aqueous ammonia, a solid compound is formed, which is the amide of ricinolic acid, or *Ricinolamide*, $C_{36}H_{35}NO_4$. It is white; crystallises in mammellated masses; fuses at 66° C.; is insoluble in water, but soluble in alcohol and ether; and burns with a very smoky flame. It is not attacked by potash in the cold, but when boiled with a strong solution of potash, it gives off ammonia, and is converted into ricinolate of potash.

The ricinolic acid obtained by this process of saponification has the composition $C_{36}H_{34}O_6$; other products however are formed at the same time. The action does not take place till the potash parts with its water, and begins to fuse. A volatile liquid is then given off; and if the mass be afterwards dissolved in water, and the solution treated with hydrochloric acid, a mixture of two oily acids, one liquid and the other solid, rises to the surface. The liquid portion is ricinolic acid, and the solid portion *sebacic acid*, $C_{20}H_{18}O_8$. The latter is not contained in the ricinolamide, but is produced, together with the volatile oil above-mentioned, by the decomposition of the ricinolic acid.

The sebacic acid and the volatile liquid may, however, be much more conveniently obtained by simply heating castor-oil with a very strong solution of potash (or better, with the solid hydrate). A volatile oil having an agreeable aromatic odour is then given off, in quantity amounting to one-fifth of the castor-oil employed, and sebate of potash remains in the retort.

The volatile oil is transparent; stains paper like essential oils; is insoluble in water, but soluble in alcohol, ether and acetic acid; and burns with a very beautiful white flame. Its density is 0·823 at 19°, and boiling-point 180° C. Its composition is expressed by the formula

$$C_{16}H_{18}O_2.$$

The theoretical density of its vapour is 4·49; experiment gives 4·50 = 4 volumes.

Sulphuric acid dissolves it, and the mixture forms crystallisable salts with lime and baryta. When heated with sulphuric acid, it is transformed into a hydrocarbon $C_{16}H_{16}$, which is very fluid, lighter than water, burns with a very brilliant flame, boils without decomposition at 125°, and forms a vapour, whose density is by calculation 3·86, by experiment 3·90 = 4 volumes. Fused chloride of zinc con-

* Compt. Rend. XXXIII, 141.

verts the volatile oil into a mixture of several isomeric hydrocarbons, the most abundant and volatile of which is identical with that formed by the action of sulphuric acid. Chloride of calcium dissolves in the volatile oil, and the solution yields very beautiful transparent crystals, which are decomposed by heat and by the action of water. The compound is less soluble at high than at low temperatures. The action of nitric acid varies with its strength; by long continued digestion with dilute nitric acid, the oil is converted into pimelic, lipic, succinic and butyric acids.—Acetic and hydrochloric acid convert it into ethers, having very aromatic fruity odours.—Quick lime at a high temperature, transforms the oil into free hydrogen and gaseous hydrocarbons.—Potash-lime or soda-lime has no action on the oil at 250° C.; but at higher temperatures, very pure hydrogen is evolved, and a volatile acid formed, which remains combined with the potash.

All these facts show that the volatile oil belongs to the class of alcohols. It is in fact, *caprylic alcohol*, and takes its place in the series between amylic and ethalic alcohol.—Its formation by the action of potash on castor-oil is represented by the following equation:

$$\underbrace{C_{36}H_{34}O_6}_{\text{Ricinolic acid.}} + 2\,(KO\,.\,HO) = \underbrace{C_{20}\begin{matrix}H_{16}\\K_2\end{matrix}O_8}_{\text{Sebate of potash.}} + \underbrace{C_{16}H_{18}O_2}_{\text{Caprylic alcohol.}} + 2\,H.$$

On certain Salts and Products of Decomposition of Comenic Acid.

By Henry How.*

This research was undertaken with the view of extending our knowledge of the polybasic organic acids, the study of which, as the author observes, has scarcely kept pace with that of other classes of organic bodies.

Comenic acid was discovered by Robiquet,† who observed that meconic acid undergoes a change of properties when boiled with water, carbonic acid being evolved, and a product obtained, to which he gave the name of *parameconic acid*, indicative of isomerism with the original substance. Liebig,‡ however, pointed out that there was also difference in composition, and proposed the provisional name, *metameconic acid*, for the new substance, whose composition he

* Trans. Roy. Soc. of Edinb. XX, 225.
† Ann. Ch. Phys. [2] LI, 244. ‡ Ibid. LIV, 26.

represented by the formula $C_{12} H_4 O_{10}$, derived from the analysis of the acid itself, and of a silver-salt. In a subsequent paper* he showed its bibasic nature, and entered fully into the relations which this acid, now called *comenic acid*, bears to meconic acid and to parameconic acid, the product of dry distillation common to both the former bodies. The subject has been further discussed by Dr. Stenhouse, in a paper published in the first volume of the "Memoirs and Proceedings of the Chemical Society."

The comenic acid used in the author's experiments was prepared by boiling crude meconate of lime (or, still better, the acid-salt obtained by once treating this substance with boiling water and hydrochloric acid) with a quantity of tolerably strong hydrochloric acid, sufficient to dissolve it, whereby the acid was obtained in hard crystalline grains of a very dark colour. This crude product was purified by boiling it in water, with gradual addition of caustic ammonia sufficient to dissolve it—care being taken not to add an excess—and immediately filtering the liquid, which, on cooling deposited bicomenate of ammonia in hard yellow crystals if left at rest, but in soft silky prisms if agitated; in the latter state the salt is difficult to wash. By two or three crystallizations from boiling water, it is obtained in fine, radiated, four-sided prisms of dazzling whiteness; and on treating the solution of this purified salt with strong hydrochloric acid, comenic acid is precipitated in the form of a white heavy crystalline powder, which adheres to the sides of the vessel. A saturated solution of this powder in boiling water, in which it is not very soluble, deposits the acid in grains and crusts almost colourless; but as the solution cools, groups of short, prismatic, or almost leaf-like crystals appear, always possessing a characteristic yellowish-red tinge.

SALTS OF COMENIC ACID.

Bicomenate of Ammonia.—This salt was analyzed by Dr. Stenhouse, who prepared it by dissolving the acid in a slight excess of ammonia, and evaporating *in vacuo* over sulphuric acid. He found it to contain 2 equivs. of water of crystallization, which were given off at 212°, making the formula of the hydrated salt,

$$NH_4 O . HO . C_{12} H_2 O_8 + 2 Aq.$$

The salt obtained by the preceding process agrees with this formula: it is in the form of square prismatic crystals, white, and of great brilliancy, very soluble in boiling water, slightly soluble in alcohol. It has a strongly acid reaction, and is deposited even from a solution of the acid in excess of hot caustic ammonia, if the boiling has not been long continued. A salt containing an additional atom

* Ann. Ch. Pharm. XXVI.

of water is obtained by adding strong alcohol to a cold saturated solution of comenic acid in ammonia; it falls in groups of radiated prisms.

Bicomenate of ammonia in the dry state sustains a temperature of 350° F., without decomposition or loss of weight; but when heated to 390° in a closed tube, it blackens and fuses, and undergoes a change which will be described further on.

Bicomenate of Potash.—Comenic acid dissolves readily in a slight excess of potash, and the liquid, on cooling, deposits a salt which, when washed with cold water, and subsequently recrystallized from the same menstruum at a boiling heat, assumes the form of short, square, prismatic needles. They are anhydrous, and have a strongly acid reaction. Their analysis gave results agreeing with the formula,

$$KO \,.\, HO \,.\, C_{12}\, H_2\, O_8.$$

Bicomenate of Soda.—When comenic acid is dissolved in a tolerably strong and boiling solution of caustic soda, the liquid on cooling deposits two forms of crystals, one in mammellated masses, the other in transparent prisms half an inch long. On washing the mixture with a little cold water, and redissolving in boiling water, no deposit is obtained, even after the lapse of some hours; but on evaporating the liquid to two-thirds of its bulk, groups of mammillary crystals appear, which when magnified, are found to consist of four-sided elongated prisms. It appears then that bicomenate of soda is much more soluble than the corresponding potash and ammonia salts, and cannot be advantageously employed in the preparation of comenic acid. It has an acid reaction, and is anhydrous. The proportion of soda corresponds to the formula,

$$NaO \,.\, HO \,.\, C_{12}\, H_2\, O_8.$$

Neutral salts of comenic acid, with the fixed alkalies and with ammonia, do not appear to exist in the dry state. With the alkaline earths, however, the case is different.

Bicomenate of Lime.—When finely powdered, comenic acid is mixed with cold water and an excess of carbonate of lime; the latter is partially decomposed with effervescence, and the liquid, when boiled and filtered, deposits a few rhombic crystals, doubtless consisting of the bicomenate. This salt, however, is much more conveniently obtained by adding a cold, saturated, aqueous solution of bicomenate of ammonia to a solution of chloride of calcium. Small brilliant crystals are then obtained, consisting of perfectly defined transparent rhombs; they dissolve readily in boiling water, and the solution on cooling yields crystals of a larger size than those first obtained. The crystals contain 7 equivs. of water of crystallization, which are not easily driven off at 212°, but are completely expelled at 250°. The formula of the salt dried at that temperature is,

$$Ca\,O \,.\, HO \,.\, C_{1}\, H_2\, O_8.$$

Neutral Comenate of Lime.—Obtained in the form of crystalline grains, when a solution of bicomenate of ammonia mixed with excess of ammonia is poured into a solution of chloride of calcium. According to the state of dilution of the liquids employed, salts are obtained, containing different quantities of water of crystallization, and differing in appearance accordingly. In all cases, however, the salts when dried at 250° give results corresponding to the formula,

$$2\,Ca\,O\,.\,C_{12}\,H_2\,O_8 + 2\,HO,$$

2 equivs. of water being retained at that temperature. When the solutions used are tolerably dilute, groups of minute prisms are obtained, which give off 5 equivs. of water in drying; hence their formula is,

$$2\,Ca\,O\,.\,C_{12}\,H_2\,O_8 + 2\,HO + 5\,Aq.$$

From very dilute solutions, small, well-defined brilliant crystals are obtained, which give off 11 equivs. of water in drying:

$$2\,CaO\,.\,C_{12}\,H_2\,O_8 + 2\,HO + 11\,Aq.$$

All these neutral salts are converted into basic compounds by simple ebullition in water.

Baryta-salts.—Carbonate of baryta is partially decomposed by comenic acid in the cold, and completely so when heated with an excess of water, the acid comenate of baryta being produced. But when the acid is boiled in water, with excess of carbonate of baryta, effervescence ensues, but the comenic acid remains undissolved, being in combination with the earth in the form of a basic salt. By double decomposition, both the neutral and acid salts are readily obtained.

Bicomenate of Baryta.—A cold, saturated, aqueous solution of bicomenate of ammonia, gives with chloride of barium an immediate precipitate, having a crystalline character; from more dilute solutions, the salt is more slowly deposited, in well-defined transparent rhombs. It is readily soluble in boiling water, and has an acid reaction. It gives off its water of crystallization at 212°, but very slowly. The dried salt fuses on ignition, and gives by analysis results agreeing with the formula,

$$BaO\,.\,HO\,.\,C_{12}\,H_2\,O_8.$$

In the crystals, 2 equivs. of this substance are combined with 13 equivs. of water.

Neutral Comenate of Baryta.—Obtained in a similar manner to the lime-salt. Strong solutions yield minute radiated crystals; but in dilute solutions, the crystals are formed gradually, and ultimately fill the whole of the liquid, presenting under those circumstances a very beautiful appearance, being arranged in separate groups, whose silky needles radiate regularly from a centre. Under the microscope, these needles present the appearance of square prismatic crystals. The salt is insoluble in boiling water, and does not give off its water

of crystallization at 212°. When dried at 250°, it is almost pyrophoric, blowing up, on ignition, in a light fiery cloud. Its formula when dried at 250°, is

$$2BaO \cdot C_{12} H_2 O_8 + 2HO.$$

The crystals contain 8 equivs. of water in addition.

The crystallized salt, when boiled in water, is converted into a basic compound, which gives off no water at 250°.

Magnesia Salts.—The acid and neutral salts are obtained by double decomposition, similarly to the lime and baryta salts. The *acid comenate of magnesia* is much more soluble than the corresponding salts of lime and baryta; when obtained from very dilute solutions by spontaneous or very slow artificial evaporation, it forms very large crystals, which, when they possess the yellow colour so apt to adhere to salts of comenic acid, very much resemble crystals of ferrocyanide of potassium. They dissolve readily in hot water, forming a strongly acid solution. The salt when dried at 240°, retains 2 equivs. of water; its composition, when thus dried, being

$$MgO \cdot HO \cdot C_{12}H_2O_8 + 2HO.$$

Neutral Comenate of Magnesia forms hard crystalline grains, made up of groups of short prismatic needles. They are insoluble in boiling water, and give off their water of crystallization at 212°, but only after long exposure. The formula of the salt thus dried is—

$$2\ MgO \cdot C_{12}H_2O_8 + 3\ HO.$$

and that of the crystals:

$$2\ MgO,\ C_{12}H_2O_8 + 3\ HO + 8\ Aq.$$

The attempt to form a salt containing 2 HO, corresponding to the neutral comenates of lime and baryta dried at 240°, was not successful.

The comenates of strontia somewhat resemble those of baryta in appearance, but are more soluble.

Comenic acid does not form an acid salt with oxide of copper, the salt containing 2 equivalents of base being obtained both by the addition of comenic acid itself and of acid comenate of ammonia to a solution of sulphate of copper.

PRODUCTS OF DECOMPOSITION OF COMENIC ACID.

By Oxidation.—Nitric acid converts comenic acid into carbonic, oxalic and hydrocyanic acids. This action is produced even by very dilute nitric acid, and is very rapid and violent when tolerably strong acid is employed.

When comenic acid is boiled with solution of persulphate of iron, a large quantity of carbonic acid is given off, and a liquid formed containing much protoxide of iron and oxalic acid.

Comenic acid does not appear to be affected by sulphurous acid or sulphuretted hydrogen.

Action of Chlorine.—Chlorocomenic Acid.—When chlorine gas is passed through water holding powdered comenic acid in suspension, a portion of the acid is dissolved, and the clear liquid, after some time, deposits the new acid in colourless prismatic crystals. The acid is, however, more conveniently obtained by passing chlorine through a solution of the ammonia-salt.

If an alkaline ammoniacal solution of comenic acid be exposed to the action of chlorine, the first result is a precipitation of the acid comenate of ammonia; but if a cold, saturated solution of the latter salt be employed, and the gas passed through it for a long time, the whole of the colour disappears, without the formation of an immediate precipitate. After the lapse of some hours, long colourless needles are deposited, the quantity of which is increased by the addition of hydrochloric acid. The mother-liquor on gentle evaporation, gradually acquires a brownish tint, which passes ultimately into a very dark brown, and the liquid then deposits a further quantity of the new acid in prismatic crystals, separate and in groups, of a brown, nearly black, lustrous appearance. The second mother-liquor contains oxalic acid in addition to the colouring matter. The colourless crystals at first obtained, were washed with cold water and recrystallized from boiling water, in which they are readily soluble; they acquired in this process a slight shade of yellow, and presented themselves in the form of short thick square prisms. When deprived of their water of crystallization by a heat of 212°, they gave on analysis results corresponding with the formula,

$$2HO \cdot C_{12}\left\{\begin{matrix} H \\ Cl \end{matrix}\right\} O_8.$$

Hence the new substance is an acid obtained by the substitution of an equivalent of hydrogen in comenic acid by an equivalent of chlorine, according to the following equation :—

$$2HO \cdot C_{12}H_2O_8 + 2Cl = HO \cdot C_{12}\left\{\begin{matrix} H \\ Cl \end{matrix}\right\} O_8 + HCl.$$

The crystals contain 3 equivs. of water of crystallization.

Chlorocomenic acid is readily soluble in hot water, less so in cold water; but in both cases, its solubility is much greater than that of comenic acid. It imparts to persalts of iron the same deep colour as meconic and comenic acids. When a piece of granulated zinc is placed in its aqueous solution, hydrogen is slowly evolved, and both zinc and hydrochloric acid are found in the liquid. Nitric acid rapidly decomposes it, with formation of hydrochloric, hydrocyanic, carbonic, and oxalic acids. When submitted to destructive distillation, it fuses and blackens, gives off hydrochloric acid in large

quantity, and towards the end of the process, a small quantity of a crystalline sublimate appears, probably consisting of pyromeconic acid.

Chlorocomenic acid is bibasic, and forms two series of salts analogous to those of comenic acid, but generally speaking possessed of greater solubility. It does not appear to form neutral salts with the alkalies. The acid salts of potash, soda, and ammonia, crystallize readily. A solution of the last-mentioned salt gives with the chlorides of calcium and barium, radiated groups of needles, which appear more or less quickly according to the state of concentration of the solutions; with sulphate of magnesia, a few crystals after some time; with sulphate of copper, a crystalline salt which separates rapidly from the liquid.

The neutral salts of these bases appear to be generally insoluble, amorphous substances.

The acid silver-salt $2(AgO \,.\, HO \,.\, C_{12}HClO_8) + 3\ Aq$, is obtained in feathery crystals by treating a warm aqueous solution of the acid with nitrate of silver. The neutral silver-salt, $2\ AgO,\ C_{12}HClO_8$ is a yellow, flocky, amorphous substance, obtained by adding a solution of the acid in a slight excess of ammonia to nitrate of silver. It is insoluble in boiling water, and acquires in the process of drying the consistence and adhesiveness of clay, which it also closely resembles in appearance.

Action of Bromine.—Bromocomenic Acid.—The action of bromine on comenic acid is analogous to that of chlorine. Comenic dissolves in bromine, yielding a colourless liquid, if the bromine is not in great excess. In the course of a few hours, the new acid is deposited in fine, square prismatic crystals, often of considerable length, and presenting a very beautiful appearance, from their high refractive power. The acid may also be obtained by the addition of bromine-water to solution of acid comenate of ammonia; but this process is not so convenient as the former.

Bromomeconic acid, when dried at 212°, is composed according to the formula,

$$2HO \,.\, C_{12}\left\{\begin{matrix} H \\ Br \end{matrix}\right\} O_8,$$

and the crystals contain 3 additional equivalents of water. This acid closely resembles chloromeconic acid in its general properties; it is, however, rather less soluble in hot water and in alcohol, and is deposited from the alcoholic solution in fine rhombic crystals. It is decomposed by zinc, and when treated with nitric acid gives off hydrobromic, hydrocyanic, carbonic, and oxalic acids. The acid ammonia-salt crystallizes in fine long needles; the acid salts of potash and soda also crystallize. No neutral salts of the alkalies could be formed. The acid salts of the alkaline earths are very soluble; the neutral salts, insoluble and amorphous. The acid silver-

salt is obtained in the form of a flocculent precipitate, by adding an aqueous solution of bromocomenic acid to an aqueous solution of nitrate of silver. It is soluble in boiling water, and is deposited from the solution in brilliant, short, prismatic crystals. The neutral silver-salt is obtained as a yellow amorphous precipitate on adding a solution of the acid in a slight excess of ammonia to nitrate of silver; when dried, it presented the same clayey character as the chlorocomenate. Iodine does not appear to decompose comenic acid.

Comenovinic Acid.—When comenic acid, in the state of fine powder, is suspended in absolute alcohol, in which it is insoluble *per se*, and a stream of dry hydrochloric acid passed through the liquid, the whole or the greater part of the acid is slowly taken up. The clear solution, when evaporated to dryness at a temperature somewhat below 212°, leaves a crystalline residue, which, when freed from adhering hydrochloric acid by gentle heating, and recrystallized from water below the boiling point, yields well-defined, square prismatic needles of considerable size. These crystals, dried *in vacuo*, and analysed, gave results corresponding to the formula, $C_{16}\,H_8\,O_{10}$, or

$$HO\,.\,C_4\,H_5\,O\,.\,C_{12}\,H_2\,O_8.$$

The new substance is, therefore, *Comenovinic* acid, and analogous in composition to sulphovinic, tartrovinic acid, &c. The crystals are anhydrous.

Comenovinic acid is readily soluble in hot water, and may be boiled for a short time without decomposition; but if long kept at this temperature, it is decomposed, and comenic acid produced. It is extremely soluble in alcohol. In the dry state, it begins to volatilize at 212°. At 275°, it fuses into a transparent brownish liquid, which, on cooling, becomes a crystalline striated mass. When kept at a temperature near its melting point, it sublimes, unaltered in composition, in brilliant, long, flattened prisms of great beauty. It is strongly acid to test-paper. Its aqueous solution readily coagulates white of egg, and imparts a deep red colour to persalts of iron.

Comenovinic acid rapidly decomposes in contact with fixed bases; hence the author has not been able to obtain any of its salts in the dry state. The ammonia-salt is obtained in silky yellow tufts, by passing dry ammoniacal gas into a solution of the acid in absolute alcohol; it preserves its silky appearance when dried, but soon begins to give off ammonia in a dry atmosphere. The comenovinates of the alkalies and alkaline earths are very soluble. The silver-salt is gelatinous, and decomposes rapidly, even in the dark.

DECOMPOSITION OF COMENATE OF AMMONIA.

Comenamic Acid.—When a solution of comenate of ammonia containing an excess of alkali is boiled, it soon becomes coloured, and after some time a black-red fluid is obtained. If the boiling be con-

tinued till the whole or the greater part of the ammonia is expelled, and the liquid then allowed to cool, a grey sediment falls down, which, when thrown on a filter, is found to have a most peculiar, clayey, tenacious character. It is the ammonia-salt of comenamic acid, much contaminated by adhering colouring matter. It dissolves, though sparingly, in boiling water, and hydrochloric acid added in just sufficient quantity to decompose it, precipitates the acid in very dark, bronze-coloured scales, which separate completely as the liquid cools. The crystals may be readily decolorized by two or three crystallizations from boiling water, or better, by means of animal charcoal free from iron.

The pure crystals, dried at 212°, gave results corresponding to the formula, $C_{12} H_5 O_8 N$; whence it appears that the new substance is an acid amide, analogous to oxamic acid, and its constitution is expressed by the formula of acid comenate of ammonia *minus* 2 atoms of water:

$$HO . NH_2 . C_{12} H_2 O_7.$$

The crystals contain 4 atoms of water of crystallization.

Comenamic acid is likewise formed when bicomenate of ammonia is heated to 390° Fahr. in a sealed tube. A black coaly mass is then obtained, partly soluble in boiling water; and the filtered liquid treated with hydrochloric acid yields comenamic acid, in the form of a white, scaly precipitate.

The acid, as obtained by the first process, forms brilliant scales, very slightly soluble in cold water; they effloresce and lose their lustre in a dry atmosphere. It is soluble in boiling spirit, but very slightly in absolute alcohol. It has a strong acid reaction, dissolves readily in excess of alkali, and with extreme facility in the strong mineral acids. From a solution in any of these acids, ammonia added in quantity not quite sufficient to neutralize the whole of the solvent, throws down a granular precipitate of the ammonia-salt. The aqueous solution of comenamic acid imparts to persalts of iron a magnificent and deep pure purple colour, which is destroyed by a few drops of mineral acid, but reappears on dilution with water. Comenamic acid is decomposed by boiling with caustic potash, with evolution of ammonia and production of comenic acid.

With a certain proportion of potash, soda, or ammonia, comenamic acid forms crystallizable salts, which have an acid reaction. The formula of the ammonia-salt is:

$$NH_4 O. C_{12} H_4 NO_7.$$

Comenamic acid dissolves the earthy carbonates with effervescence. When the acid is in excess, a crystalline salt with an acid reaction is obtained; but with an excess of carbonate nearly all the acid remains undissolved, in the form of a basic compound.

A solution of the crystalline ammonia-salt gives with nitrate of

silver a white gelatinous precipitate, partially decomposed by boiling water. The same solution, made alkaline, gives with nitrate of silver a yellow, flocky precipitate, which almost instantly begins to darken in colour, and ultimately becomes black and amorphous. The same solutions give with acetate of lead heavy insoluble precipitates; the acid solution gives with sulphate of copper a grey precipitate.

By adding a solution of the ammonia-salt to chloride of barium, a crystalline salt was obtained, having the composition, $BaO . C_{12} H_6 NO_9$; and, supposing it to be the neutral salt of a monobasic acid, it may be expressed by the formula:

$$BaO . C_{12} H_4 NO_7 + 2HO.$$

By treating an alkaline solution of the ammonia-salt with chloride of barium, a heavy white powder is obtained, insoluble in boiling water, and composed of $2BaO . C_{12} H_5 NO_8$. To assimilate this salt to the last, it must be regarded as a basic compound, in which one of the equivalents of water retained at 212° is replaced by baryta; thus:

$$BaO . C_{12} H_4 NO_7 + BaO . HO.$$

As precipitated from water, it retains an additional equivalent of water.

The lime-salts are very similar in appearance to the baryta-salts: and with every base this acid seems to form two salts, which is a curious fact, since, reasoning from analogy, a substance originating as it does should be monobasic in its character. In conclusion, the author mentions that he has noticed in the behaviour of comenamic acid, under certain circumstances, phenomena which are likely to repay further investigation.

On a New Source for Obtaining Capric Acid, and Remarks on some of its Salts.

By T. H. Rowney.*

Capric acid has been obtained from various sources. Chevreul and Lerch discovered it in the butter of the cow and goat; Redtenbacher, among the volatile oily acids which he obtained by acting upon oleic acid with nitric acid; Gerhardt and Cahours produced it by the action of nitric acid upon oil of rue; and Görgey found it in cocoa-nut oil. From all these sources, however, it has been obtained in small quantity only, and always mixed with other acids of the same series.

The new source from which Mr. Rowney has obtained this acid is the fusel-oil or grain-oil, of the Scotch distilleries. This oil chiefly

* Trans. Roy. Soc. Edinb. XX, 219.

consists of water, alcohol, and the hydrated oxide of amyl, in various proportions, but sometimes contains small quantities of other constituents: thus, œnanthic ether was found in it by Mulder, and margaric acid by Kolbe. The oil examined by Mr. Rowney was found to contain capric acid, probably in combination with oxide of amyl.

On subjecting the grain-oil to fractional distillation, the first portions which passed over consisted chiefly of water and alcohol, with a little hydrated oxide of amyl; the second portion was composed of the latter substance nearly pure; and a dark-coloured residue was left, which had a disagreeable odour, was insoluble in water and carbonate of potash, but was rendered soluble in water by boiling with a strong solution of caustic potash, amylic alcohol being at the same time given off. Digestion for two or three days on a sand-bath with strong solution of potash, likewise renders the oil soluble in water. On adding hydrochloric or sulphuric acid to the cold alkaline solution, a dark oily mass consisting of impure capric acid rises to the surface. To purify this product, it was dissolved in dilute ammonia, after filtering and washing with cold water; the solution mixed with chloride af barium; the resulting precipitate filtered and washed with cold water; afterwards dissolved by boiling water; and the solution filtered whilst hot, and then left to crystallise. The baryta-salt thus obtained was purified by two or three crystallisations, then decomposed by carbonate of soda, and dilute sulphuric acid added to the filtrate to separate the capric acid. The product was solid, and nearly colourless; but to obtain it perfectly pure, it was dissolved in alcohol, and the solution mixed with a large quantity of water, whereupon it became turbid, and after some hours deposited capric acid in the crystalline state. By repeating this process, the acid was obtained quite pure and colourless. The mother-liquors from the baryta-salt yielded a further portion of capric acid, together with an oily acid, the quantity of which was, however, too small to allow of its constitution being determined.

Capric acid thus obtained is a solid white, crystalline compound, which has a faint odour, and fuses readily between the fingers. It is very soluble in ether and alcohol, and does not crystallise from these solutions. It is insoluble in cold water, but dissolves sparingly in boiling water, and crystallises from the solution on cooling in the form of scales. It is also dissolved without decomposition by strong boiling nitric acid, and is precipitated from the solution by water. From the alcoholic solution, it is obtained, by the addition of water, in a mass of needle-shaped crystals. It is lighter than water. The crystallised acid begins to fuse at 81° F., but the temperature rises to 116° before the fusion is complete. The fused acid is slightly coloured, has a faint odour, and becomes crystalline on cooling. The crystallised acid, dried *in vacuo*, gave by analysis results agreeing with the formula $C_{20}H_{20}O_4$.

Caprate of silver, $C_{20}H_{19}AgO_4$, is obtained by adding nitrate of silver to an ammoniacal solution of capric acid. It is insoluble in cold water, sparingly soluble in boiling water, and is deposited from the solution, in needle-shaped crystals, on cooling. It is more soluble in boiling alcohol; but the solution becomes dark-coloured, and the crystals obtained from it are also dark-coloured. It is very soluble in ammonia, and if the ammoniacal solution be kept in a warm place, so as to drive off the ammonia, a crystalline salt is obtained. Caprate of silver blackens rapidly, if exposed to bright daylight while moist, but after drying the light no longer affects it.

Caprate of baryta, $C_{20}H_{19}BaO_4$, is obtained by adding chloride of barium to an ammoniacal solution of capric acid. It is soluble both in water and in alcohol at the boiling-points, and crystallises out, on cooling, in needle-shaped crystals. This salt, as well as the salts of the other alkaline earths, and the silver-salt, are insoluble in water after having been dried, because they float on the surface of the water and repel it; but if first moistened with alcohol, they may be again rendered soluble in boiling water. They are also very difficult to pulverise.

The *caprates of lime* and *magnesia* are similar to the baryta-salt, but more soluble in alcohol and boiling water. The quantity of base in the magnesia-salt agrees with the formula $C_{20}H_{19}MgO_4$; the lime-salt was not analysed.

The other salts of capric acid do not crystallise readily. The copper-salt is insoluble in water and alcohol, but soluble in ammonia. The lead-salt is insoluble in water, and very sparingly soluble in boiling alcohol, which deposits it in rounded grains on cooling. The soda-salt is exceedingly soluble both in water and alcohol, and does not crystallise from these solutions; when evaporated to dryness, it forms a hairy mass, partially crystalline on the surface. None of these salts could be obtained in a state of purity, and their analyses gave an excess of base; but the copper and soda-salts appear to be neutral.

Capric ether was obtained by dissolving the capric acid in absolute alcohol, passing dry hydrochloric acid gas into the solution to saturation, and then adding water, which caused the capric ether to rise to the surface in the form of an oily liquid. After washing with cold water, and drying with chloride of calcium, it had a density of 0·862. It is insoluble in cold water, but readily soluble in alcohol and ether. The quantity obtained was too small for analysis.

Capramide.—The capric ether was converted into this compound by solution in alcohol and long-continued digestion in a stoppered bottle with strong ammonia. After a few days, the solution became turbid, and subsequently crystals made their appearance. The digestion was continued till the whole of the ether had disappeared, after which the solution was separated from the crystals by filtration; the filtrate evaporated to dryness over the water-bath; the residue

dissolved in alcohol; and the solution mixed with water, which caused the capramide to crystallise; the whole was then dissolved in warm dilute alcohol, and allowed to crystallise. Capramide thus obtained is quite colourless, and crystallises in brilliant scales, which, when dry have a bright silvery lustre. It fuses below 212°, is insoluble in water and ammonia, very soluble in cold alcohol, and also in dilute alcohol when warmed with it. Analysis gave results in accordance with the formula $C_{20} H_{21} O_2 N$.

Chemical Report on the Supply of Water to the Metropolis.

Letter from the Right Hon. Sir George Grey, Bart., Principal Secretary of State for the Home Department.

Whitehall, 23rd January, 1851.

GENTLEMEN,

I herewith transmit to you a copy of the Report of the General Board of Health on the Supply of Water to the Metropolis, together with the Appendices containing the Evidence on which the Report is founded, and some other Papers printed by the Board in connection with this subject.

I also transmit a copy of the Evidence taken before the Select Committee of the House of Commons, during the Session of 1850, on the River Lea Trust Bill.

I have to request that after a consideration of these Documents you will report to me, for the information of the Government, your opinion upon the following Questions, namely:

What is the chemical quality of the various waters which are now supplied to the metropolis?

What is the chemical quality of the water derived from the sources whence the Board of Health propose to supply the metropolis?

What is the chemical quality of the water proposed to be supplied from Watford?

Whether if the quality of the water now supplied be objectionable, any remedy can be applied by filtration, or otherwise, without abandoning the present sources of supply?

Whether if soft water were to be obtained in sufficient quantity for the supply of the metropolis, any comparative inconvenience would arise from the use of such water under the present system of

distribution, and if so, whether available means may be found of obviating it?

What are the properties to be preferred in the water selected for the supply of the metropolis?

As much information upon this subject has been collected in the Papers now transmitted to you, I hope that you may be enabled to form your opinion without the delay which would be incurred by the taking of additional evidence, but it will be competent to you, if you think it necessary, to ask for further explanations from any of the parties who have already given evidence upon the subject, or to call for information from other parties.

I have the honour to be,

Gentlemen,

Your obedient servant,

G. GREY.

THOMAS GRAHAM, ESQ., F.R.S.,
W. A. MILLER, M.D., F.R.S.,
A. W. HOFMANN, Ph.D., F.R. .

REPORT.

SIR,

We have the honour to report to you our opinions on the Questions respecting the Metropolitan Water Supply, which are proposed for our consideration in your letter addressed to us of the 23rd of January last, as follows:

I.—OF THE CHEMICAL QUALITY OF THE PRESENT SUPPLY.

It appeared unnecessary to include in this inquiry the water drawn from the shallow wells sunk into the superficial strata within the confines of the metropolis, as the supply from these wells is insignificant, and in the course of still farther diminution in quantity, and often of deterioration in quality from obvious causes. The deep well-water also obtained by penetrating through the great clay beds to the chalk below, although of importance to the proprietors of breweries and to other manufacturers, who have incurred the expense of sinking wells on their premises, is of comparatively little general interest, as this source of supply is not expansive and appears to be already fully appropriated. It is to the chemical quality of the water furnished to the metropolis by the several water companies that we shall, therefore, confine our observations under the present head.

The existing Metropolitan Water Companies with their estimated delivery per day are as follows:*

		Gallons per day.
Water derived from the Thames 19,907,480 gallons.	Grand Junction Company	3,541,717
	West Middlesex	3,334,054
	Chelsea	3,940,730
	Southwark and Vauxhall	6,013,716
	Lambeth	3,077,260
Water derived from other sources than the Thames 25,978,445 gallons.	New River	15,435,617
	East London	9,036,049
	Kent	1,079,311
	Hampstead	427,468
		45,885,925

It thus appears that of a daily supply of nearly 46 million gallons, 20 million gallons are taken from the Thames, and 26 million gallons are obtained from other sources.

These latter sources are, for the New River Company, Chadwell Spring, in the chalk strata, near Ware, the river Lea above Ware, Spital-brook and other small springs taken into the River; the water-shed of the North-hall district, and four deep wells sunk into the chalk in Middlesex and Hertfordshire (two being in Great Amwell). The supply of the New River Company from the Lea is at present limited to 1340 cubic feet per minute. But the River Lea Navigation Trustees have applied to Parliament for powers to construct reservoirs on the upper part of the Lea, and upon its tributaries the Rib and Ash, in order to enable the trustees to increase the New River supply.

Of the East London Company, the supply is taken from the Lea at a point six miles from its mouth at Bow Creek, and two miles beyond reach of the tidal waters of the Thames, which ascend some distance up the River Lea.

The Kent Company, which supplies Deptford, Greenwich and Woolwich, takes its supply from the Ravensbourne below Lewisham.

Hampstead; springs at Hampstead, Caen Wood, two artesian wells, and (temporarily) the New River.

Of the Thames companies, the Lambeth at present takes its water at Lambeth, the lowest point at which water is drawn from the river. But this company will very shortly be supplied from their new works at Thames Ditton, near Kingston, which is a higher source than any other Thames company possesses.

The Chelsea and the Southwark-Vauxhall Companies, from near the Red House, Battersea, above Vauxhall Bridge.

The West Middlesex, from near Barnes Terrace in the parish of

* Calculated from the last returns made by the Water Companies to the General Board of Health, and communicated to this Commission, with much other valuable information, by the Board.

Barnes; and the Grand Junction a little way higher up, 360 yards above Kew Bridge.

Of these points on the river from which water is drawn, it may be said that those of the Lambeth, Chelsea and Southwark-Vauxhall works are within reach of the return tidal flow of the Thames from London Bridge, while the sources of the Grand Junction and West Middlesex appear to be above the influence of the returning tide from any point so low as to receive a share of the London drainage. It should be, added, however, that in a favourable state of the tide, a very sensible improvement in the appearance of the Thames is observed above Vauxhall Bridge, and that the river there begins to assume the character which it maintains up to Richmond. The whole Thames Water Companies draw from this improved section of the river, except the Lambeth Company, which will soon be otherwise supplied.

Specimens of the water of all the Companies were taken for analysis, always from a main and generally at the nearest accessible point to the works of the Company, or to a distributing reservoir. They were all drawn on the 29th, 30th and 31st of January last, after moderately rainy weather, with the river full but not flooded. The specimens may be considered as representing the least favourable state of the water supply to the metropolis during winter, but still such as it may continue for several months in a wet season like the last. The temperature of the river at the time was 44° Fahr.

The results are given in two forms, first the acids and bases separately, as actually found by analysis, and secondly the same acids and bases arranged in the form of salts, or chemically combined as they are believed to exist in the waters.

The first group consists of waters not derived from the Thames.

1. ANALYSES OF THE NEW RIVER, EAST LONDON, KENT AND HAMPSTEAD WATERS.

	New River Water Company.	East London Water Company.	Kent Water Company.	Hampstead Water Company.
	Grains in an Imperial Gallon.			
Lime	5·7192	6·9034	7·82	2·9160
Magnesia	0·5280	0·7336	0·62	1·7098
Potassium	0·4972	0·5600	0·35	1·6471
Sodium	1·1634	0·9989	0·86	7·5761
Iron, alumina and phosphates	trace	0·4760	trace	trace
Sulphuric acid (SO_3)	3·2550	2·5830	1·86	9·1702
Chlorine	1·0500	1·0682	1·52	4·1230
Carbonic acid	11·1020	11·4527	11·56	10·9823
Silica	0·5005	0·6216	0·49	0·0728
Nitric acid	0·0150	0·4800	„	0·050
Ammonia	trace	trace	trace	trace

2. ANALYSES OF THE NEW RIVER, EAST LONDON, KENT AND HAMPSTEAD WATERS.

	New River Water Company.	East London Water Company.	Kent Water Company.	Hampstead Water Company.
	Grains in an Imperial Gallon.			
Carbonate of lime	7·82	10·16	11·64	4·95
Sulphate of lime	3·23	2·33	3.16	„
Nitrate of lime	0·02	0·72	„	0·07
Carbonate of magnesia	1·09	1·51	1·28	3·53
Chloride of sodium	1·73	1·76	2·24	6·79
Sulphate of soda	1·49	0·94	„	15·14
Chloride of potassium	„	„	0·66	„
Sulphate of potassa	1·11	1·25	„	1·40
Carbonate of potassa	„	„	„	1·80
Silica	0·50	0·62	0·49	0·07
Iron, alumina and phosphates	traces	0·47	traces	traces
Ammonia	traces	traces	traces	traces
Organic matter	2·79	4·12	2·61	1·84
Total	19·78	23·88	21·08	35·59
Solid residue obtained on evaporation	19·50	23·51	29·71	35·41
Free carbonic acid in cubic inches at 44° F.	14·49	12·38	10·15	13·30
Free carbonic acid grains in a gallon	7·24	6·19	5·07	6·67
Suspended matter	1·49	1·07	„	0·52
Degree of hardness (Clark's scale)	14°·9	15°·0	16°·0	9°·8

The second group is composed of the Thames waters.

1. ANALYSES OF THAMES WATERS.

	Water taken at Thames Ditton.	Grand Junction, supplied at Kew.	West Middlesex, supplied at Barnes.	Chelsea Company, near Red-House, Battersea.	Southwark and Vauxhall Company, near Red-House, Battersea.	Lambeth Company, supplied at Lambeth.
	Grains in the Imperial Gallon.					
Lime	8·0046	7·4522	7·5390	7·5117	7·2751	6·7970
Magnesia	0·6070	0·5544	0·5628	0·5527	0·6020	0·7011
Potassium	0·4261	0·2769	0·2185	0·2821	0·6048	0·4291
Sodium	0·4330	0·6127	0·7387	0·5784	0·7861	0·7805
Iron, alumina and phosphates	0·0940	0·7630	0·7630	0·2910	0·3430	0·8505
Sulphuric acid	1·8782	2·6460	3·0380	3·3005	2·4150	2·2015
Chlorine	0·9890	0·8512	1·1424	1·2229	1·1725	1·1746
Carbonic acid	14·2170	11·9826	10·6260	10·6470	12·1100	12·8520
Silica	0·6290	0·4466	1·0013	0·7189	0·7679	1·0451
Nitric acid	0·0180	trace	trace	trace	0·2360	trace
Ammonia	trace	trace	trace	trace	0·0309	trace

2. ANALYSES OF THAMES WATERS.

	Water taken at Thames Ditton	Grand Junction Company, supplied at Kew.	West Middlesex Company, supplied at Barnes.	Chelsea Company, supplied at Red-House, Battersea.	Southwark and Vauxhall Company, supplied at Red-House, Battersea.	Lambeth Company, supplied at Lambeth.
	Grains in the Imperial Gallon.					
Carbonate of lime	11·79	10·90	9·94	9·28	10·57	8·99
Sulphate of lime	3·06	3·26	4·78	5·61	3·05	2·99
Nitrate of lime	0·27	trace	trace	trace	0·35	trace
Carbonate of magnesia	1·27	1·17	1·16	1·08	1·29	1·44
Chloride of sodium	1·10	1·40	1·88	1·47	1·99	1·95
Sulphate of soda	,,	0·18	,,	,,	,,	,,
Chloride of potassium	0·67	,,	,,	0·55	,,	,,
Sulphate of potassa	0·17	0·61	0·48	,,	1·34	0·95
Silica	0·62	0·44	1·00	0·71	0·76	1·04
Iron, alumina and phosphates	0·09	0·67	0·76	0·29	0·34	0·85
Ammonia	trace	trace	trace	trace	0·03	trace
Organic matter	2·29	3·07	2·75	2·38	1·51	2·59
Total	21·33	21·70	22·75	21·37	21·23	20·80
Solid residue found on evaporation	20·78	21·72	22·67	21·28	21·08	20·40
Free carbonic acid in cubic inches, at 44° F.	16·89	13·46	11·56	12·30	13·57	16·64
Free carbonic acid, grains in gallon	8·25	6·73	5·78	6·15	6·78	8·32
Suspended matter	,,	0·01	0·02	,,	1·92	1·15
Degree of hardness (Clark's scale)	14·22	14·00	14·60	14·44	15·00	14·16

The waters were all sensibly tinged of a yellow or ochry tint, due chiefly to suspended clay, with the exception of the Kent water, which was clear and bright. This turbid condition of the waters was represented to us as having subsisted for two months, but was rather on the decline at the time of observation. It was least marked in the Chelsea, Grand Junction and West Middlesex waters, which are filtered by the companies. These waters did not allow the suspended matter to fall entirely on standing in a glass jar, but remained sensibly coloured after several weeks of rest; they might all, however, we believe, be perfectly clarified by the use of a properly constructed house-filter. The Thames Ditton water was taken from a main in Surbiton, near the company's works, at a later period of the season than the others, namely, on the 22nd of February, and was clear and bright. It is a filtered water.

The soluble organic matter from two of the Thames waters was submitted to ultimate analysis, and found to give 0·105 grain of nitrogen in the Grand Junction Water, and 0·031 grain of nitrogen in the Southwark and Vauxhall Water. The existence of nitrogen is generally supposed to imply the animal origin of organic matter, and on such evidence a minute and probably unimportant portion of animal organic matter would be admitted to be present.

None of the waters had any marked taste or odour, nor betrayed any indication of putrescence, either when first taken up or after being kept in bottles for several weeks at a temperature between 50° and 60°; nor even after remaining in close vessels for two weeks at 80°.

In these waters when submitted to microscopic examination no animalcules were observed in any case. But the period of the year was not that at which any considerable development of animal life is to be looked for.

All the waters under consideration have much of a common character, arising from the similar geological conditions of their sources. Every one of them is derived in a great proportion from the Chalk Formation, of which the waters have peculiar properties. This appears, both in the degree and the nature of the hardness they exhibit, which is due to the presence of salts of lime and magnesia in solution.

It may be useful to distinguish the quality known as the "hardness" of water, according as it is of a *temporary* or *permanent* character. Perfectly pure or soft water, when exposed to contact with chalk (carbonate of lime) is capable of dissolving only a very minute quantity of that substance; one gallon of water, in weight equal to 70,000 grains, taking up no more than 2 grains of carbonate of lime. This earthy impregnation is said to give the water 2 degrees of hardness. But waters are often found containing a much larger quantity of carbonate of lime, such as 12, 16, or even 20 grains and upwards in the gallon. In such cases the true solvent of the carbonate of lime, or at least of the excess above 2 grains, is carbonic acid gas, which is found to some extent in all natural waters. But this gas may be driven off by boiling the water, and the whole carbonate of lime then precipitates in consequence, or falls out of the water, with the exception of the 2 grains which are held in solution by the water itself. The gas-dissolved carbonate of lime gives, therefore, *temporary* hardness curable by boiling the water. An artificially prepared hard water, containing 13½ grains of carbonate of lime to the gallon, was observed to decrease from 13·5 to 11·2 degrees of hardness, merely by heating it in a kettle to the boiling point. Boiling for five minutes reduced the hardness to 6·3 degrees, fifteen minutes to 4·4 degrees, thirty minutes to 2·6 degrees, and one hour to 2·4 degrees. The softening effect of boiling does not therefore appear all at once, but the greatest proportional effect is certainly produced by the first five minutes' boiling. The West Middlesex and New River waters were both found to soften by boiling, very much in the same manner as the preceding pure chalk water, except that the ultimate hardness of the two waters specified was somewhat

higher. By an hour's boiling, the West Middlesex fell from 14·6 to 5·5 degrees, and the New River from 14·7 to 4·1 degrees.

Other salts of lime, such as sulphate of lime, are generally dissolved in water without the intervention of carbonic acid gas, and therefore remain in solution although the water is boiled, imparting *permanent* hardness. The shallow wells in the gravel all round London are permanently hard to the extent of 15 degrees and upwards, from the presence of earthy sulphate, and contrast disadvantageously in this respect with the river waters.

The carbonate of lime in water decomposes about ten times its weight of soap, in washing (more exactly 8·8 white curd soap and 10·7 common yellow soap), and other salts of lime act injuriously upon soap, in proportion to the lime they contain; the soluble soap containing soda being converted into an insoluble and useless compound containing lime. The water is then deprived of lime or softened at the expense of the soap. The lime in 100 gallons of Thames or of New River Water thus occasions the destruction of about 34 ounces of soap, before any portion of it becomes available as a detergent. By the experiment of adding measured quantities of a solution of soap to a certain measure of any water to be examined, till the soap begins to give a lather with the water, or soap bubbles appear on the surface on agitation, the proportion of earthy salt or degree of hardness may be ascertained; the method generally followed in the experiment being that directed by Dr. Clark.

The hardness was remarkably uniform in the water of the eight principal Metropolitan Water Companies; the Hampstead water, which is locally peculiar, and amounts only to about 1 per cent of the whole metropolitan supply, being withdrawn from the comparison.

The degrees of hardness, by Clark's soap test, of the waters of the eight principal London Companies, observed on the 29th, 30th, and 31st of January, were as follows:

From the Thames.	Grand Junction	14°·0
	West Middlesex	14°·6
	Vauxhall and Southwark	15°·0
	Chelsea	14°·4
	Lambeth	14°·2
	Lambeth (from Thames Ditton, March 8)	14°·2
From other sources than the Thames.	New River	14°·9
	East London	15°·0
	Kent	14°·0

The variation observed in this property is from 14° to 15°, or one degree only. It appears also, from observations made at different seasons, that this range is not considerably exceeded at any period of the year, except during floods, when the hardness of Thames water may fall to 8 or 9 degrees.

The general qualities of the present water supply, deduced from

observation of its ordinary properties, as well as from chemical analysis, may be thus enumerated:

1. The effect of ordinary filtration through sand is very decided on Thames water, as it appears to be upon chalk waters in general. The river water can thus be easily obtained, unless in certain exceptional circumstances, entirely free from suspended solid matter, or mechanical impurities.

2. When in good condition, the Thames water also possesses the peculiar and agreeable brightness of chalk waters, arising from the entire absence of colour, combined also usually with good aeration.

3. The Thames water may be described to be, in circumstances not unfavourable to purity and coolness, a palatable water. The amount and nature of its saline constituents probably contribute to its general acceptability as a beverage.

4. It may be safely stated, that no sufficient grounds exist for believing that the mineral contents of the water supplied to London are injurious to health. No reasonable doubt indeed can be entertained of its salubrity. The shallow well-waters of London vary from 32 to 80 degrees of hardness, yet these waters have never been pronounced unwholesome. An aerated water is manufactured and safely consumed to some extent which contains 92 grains of carbonate of lime to the gallon, instead of 12 or 14 grains, as in Thames water. The portion of lime and magnesian salts in the water drunk must indeed be greatly exceeded in general, by the quantity of the same salts which enters the system in solid food. The only observations, from which an interference of the lime in water, in deranging the processes of digestion and assimilation in susceptible constitutions, has been conjecturally inferred, have been made upon waters containing much sulphate of lime and magnesia, as the Brighton shallow well-water, or the hard selenitic water of the New Red Sandstone, and have no force as applied to the Thames and its kindred waters, as the earths exist in these principally in the form of carbonate.

5. The water at present supplied may be circulated through leaden pipes, or preserved in leaden cisterns with an unusual degree of safety. The corrosion of water cisterns in London is generally occasioned by the mud which subsides to the bottom, particularly when the sediment includes organic matter, and the evil might be greatly diminished by more frequently cleaning out the cisterns. But it is to be particularly remarked, that this corrosion is not attended by any sensible solution of lead in the water, and that the water of the cistern is not poisoned in consequence. The London water may indeed be said to exert the least degree of solvent action upon lead. To the nature of the action of different waters on this metal there will be occasion again to refer.

The circulating system of iron pipes appears also to receive a certain amount of protection from the alkaline character of the present

supply. The erosions and bulky deposits in cast-iron pipes, which have given great trouble in the distribution of certain waters, are quite unknown in London.

6. Putrefactive decomposition appears also to occur less rapidly in hard than in soft water, and hard water seems to be the more easily preserved in reservoirs or tanks without deterioration for a short time.

7. Finally, all these advantages of the present sources are enhanced by the circumstance that the attainable supply from the Thames is of remarkable uniformity, and may be said to be unlimited. The average volume of water which passes Richmond daily is calculated at 800,000,000 gallons, and the minimum at 600,000,000 gallons, the last amount being twelve times the present consumption of the metropolis, estimating the latter at 50,000,000 gallons. Although not fed by a great lake, both the Thames and the Lea are largely supplied from spongy chalk strata, which possess an enormous water-capacity, and answer the purpose of an equalizing reservoir, the discharge of water from these beds being nearly independent of the season. This must be of great service during the hot summer months, when the quality of many rivers, which depend chiefly on surface supply, becomes much deteriorated, from the effect of evaporation and the accumulation of soluble vegetable matter.

Against these grounds of commendation certain disadvantages of the present supply are to be placed.

1. The fluctuating temperature of the present supply, in which it resembles all river and surface-drainage water. The temperature of the Thames at Greenwich was observed by Mr. Glaisher to exhibit the following high range during the warm months of 1846:

In June, from 71°.9 to 73° Fahr.
In July, from 66°.1 to 67°.4 Fahr.
In August, from 66°.7 to 68°.3 Fahr.

During the months of June, July, and August, the temperature of the water supplied to the inhabitants of London is said to be generally above 65°, and sometimes above 70°. This loss of coolness in itself makes the water greatly less palatable, while it promotes the decomposition of organic matter, which farther impairs the quality of the water.

2. Like rivers generally, the Thames is liable to turbidity from floods. It then acquires a yellow colour, well known as the flood tinge, which is of an unusually persistent character, and only very partially removed by sand-filtration. We agree with engineers, who have had the fullest means of observation, in considering that so much of this discolouration is due to the compound of clay and organic matter, washed out by the Brent from the extensive and highly manured field of the London Clay Formation, which it drains,

as to make it an object to draw the London supply from a point above the *embouchure* of that tributary of the Thames, at Brentford. This clay tinge, which resists the action of acids and does not even fall down with carbonate of lime precipitated in the water, is known to be removable by alum. We were informed by an officer of one of the companies, that seven grains of alum per gallon of water would be sufficient in general to precipitate the clay completely, and to produce a perfect discolouration. The alumina is itself entirely removed, but sulphuric acid is introduced which, by converting carbonate of lime into sulphate, would induce a hardness permanent on boiling. In floods also the water often tastes disagreeably of vegetable matter.

3. Allied to this mineral discolouration is the colour and contamination to which the river is more particularly liable in the latter part of autumn and early months of winter, from the extensive decomposition of vegetable matter in the highly cultivated district through which it flows. This is one of the disadvantages which the Thames shares with all rivers, which do not originate in a barren non-retentive soil, such as the millstone grit of Lancashire, and which cannot be collected for town supply near their sources. The evil often admits of being greatly reduced by collecting from a restricted area, and storing the excess of floods in vast reservoirs, as in the new gathering grounds of several towns in Lancashire and the west of Scotland. These reservoirs, however, must be deep with an impervious bottom; and the nature and configuration of the surface afford facilities for their construction in hilly districts, which are not to be found in the valley of the Thames. For the present London supply this contamination is a serious evil.

4. As the main drain of a large and populous district, the Thames becomes at all seasons polluted by the sewerage of several considerable towns, and by the surface drainage of manured and ploughed land. Even above Kingston, a population of three-quarters of a million is found upon the banks of this river and its tributaries. The diverting the sewerage of the various towns entirely from the Thames would be attended with so much difficulty that the project need not be taken into account. At the same time, we doubt whether the existence of organic contamination from town drainage is at present perceptible in the Thames above the reach of the tidal flow, or amounts there to a sensible evil. The indefinite dilution of such matters in the vast volume of the well aerated stream is likely to lead to their destruction by oxidation, and to cause their disappearance. The river may reasonably be supposed to possess, in its self-purifying power, the means of recovery from an amount of contaminating injury equal to what it is at present exposed to in its higher section.

The contamination by sewerage, however, cannot fail to become considerable and offensive with the increase of population and the more

efficient and general drainage of towns. And it appears to be only a question of time when the sense of this violation of the river purity will decide the public mind to the entire abandonment of the Thames as a source of supply, unless indeed artificial means of purification be devised in the meantime and applied.

With reference to the possible supply of the metropolis from the upper section of the Thames, it may here be stated that a main of thirty inches in diameter is already laid for conducting water from Thames Ditton to Lambeth, capable of conveying from eight to ten million gallons daily; while arrangements are made along the whole distance for placing three additional similar pipes when required; a provision which would supply double the quantity of water now taken from the river within the tidal flow by all the existing Thames Companies.

The town-drainage below Richmond and above the tidal return from London, if at present inconsiderable, cannot be calculated to continue so, owing to the rapid extension of the metropolis in the great lines of Bayswater, Kensington and Wandsworth.

The supply of the New River and East London Companies from the Lea has all the good qualities which have been ascribed to the Thames water, to which in its mineral constituents it is essentially similar, while it appears less affected by turbidity from floods. The objectionable impregnations from town-drainage are also inconsiderable in the supply of the first of these companies. Farther, it is proposed by the River Lea Navigation Trustees to divert the town-drainage of the New River district, particularly that of Hertford, to a point on the Lea below Ware.

It has already been stated that none of the Companies' waters when taken up in January gave at the time or two weeks afterwards, when kept at either the actual temperature, or at 80°, any marked indication of putrescence to the smell or taste. The complaint on this ground is mainly to be referred to the filthy condition of the cisterns, butts, and other vessels in which the water is preserved in private houses, and is only attributable to the water companies in so far as they necessitate the use of such receptacles by furnishing an intermittent instead of a constant supply of water. It is to be feared, however, from the result of concurrent testimony, that the water does occasionally come into the houses tainted with decaying animal or vegetable matter. We have been informed, for instance, on good authority, that in a warm summer the New River water, as delivered in London, sometimes contains spawn floating in it, and has a fishy smell, which is objected to by bathers; but this matter, and all animalcules visible to the naked eye, may be detained by sand filtration, and the nuisance in this instance is to be ascribed to the omission of that practice.

Although according to chemical analysis the organic matter never

appears to rise, in the water of the Companies who filter, to a proportion by weight which need excite alarm or would appear extraordinary to the chemist, and although it may be impossible to ascertain its origin, still the balance of evidence appears adverse to the conclusion that what is known to enter is immediately destroyed. No marked increase in the proportion of nitric acid is observed in the Thames within the limits of the metropolis, which might be expected to mark the destruction by oxidation of much azotized animal matter if it really took place; while the rapid production of animalcules in Thames water when aided by light and warmth, although not in itself a source of danger, evinces the abundant presence of organic matter, which if not rapidly assimilated by these lower orders of animal beings, might render the liquid repulsive, and in all probability actively injurious to the human constitution. The antiputrescent property of Thames water, which it acquires from its hardness, is opposed to the immediate destruction of organic impurities, and is perhaps more valuable as adapting the river to the transport and removal of such matters, than for preserving the water in a condition suitable for drinking. If the Thames should continue to be the source of any considerable share of water supply, it must be desirable, therefore, to draw it at a point removed from this contamination, and entirely above the tidal flow of the river. The discolouration from the turbid floods of the Brent would at the same time be avoided, by proceeding higher up than the Teddington weir.

But, it will be asked, may not any change soon cease to be required on such grounds, when the Thames is relieved of the London sewerage, as it is anticipated that the river will be in a few years? The removal of the nuisance complained of, however, can never be complete, but only partial. The contamination from navigation and the river population must be increasing rather than otherwise; while gas-works and other indispensable chemical manufactories, which at present pour their refuse products directly into the river, would necessarily continue to do so, as these products are often of a kind not admissible into ordinary sewers.

5. The hardness of the metropolitan water-supply, which is due to its mineral constituents, may be considered as the same whether derived from the Thames or the Lea, and amounts on an average to about 14 degrees. Although this degree of hardness is considerable and highly objectionable, still it is exceeded by the hardness of pure chalk waters, such as are supplied by water companies to the towns of Gravesend, Dover and Brighton, and which may be estimated at from 18 to 20 degrees. The deposit which Thames water gives rise to in boilers is also friable and less coherent than the stony deposit from selenitic waters; and means exist, such as the use of sal ammoniac, for entirely preventing the occurrence, in steam boilers, of deposit from chalk but not from selenitic waters.

The hardness of the London water is also of the least objectionable kind, being chiefly, as has been already stated, temporary hardness, which is removed by boiling. The whole 14 degrees of hardness can be ascribed only to that portion of the water which is used cold. To ascertain the average state of hardness of heated water, portions of water were drawn on six different occasions from the fixed boiler of a kitchen range, supplied with New River water; the hardness was found to be 5·4, 4·9, 4·1, 4·1, 4·9 and 5·3 degrees, of which the mean is 4·8 degrees. The hardness of London water, as it is commonly used after boiling, appears, therefore, to be about 5 degrees, while without heating it amounts to 14 degrees. The distinction between permanent and temporary hardness was illustrated to us at Greenwich, where the brewer described the deep well-water of the Hospital (which is only occasionally pumped up) as a soft water, although its hardness is 21 degrees; but it is only used by him for mashing after being boiled, when, being a pure chalk water, its hardness is reduced to about 4 degrees. The importance of this distinction was likewise shown though in another manner at Whitehaven, where a great and apparently disproportionate advantage has been experienced, from a change in the town supply, from a water which we found to be of 6·7 degrees of hardness to another water of 1·4 degrees. The hardness of the former water, however, although not great in amount, proved to be of the permanent description; as after an hour's boiling the water of the old supply was still of 6·4 degrees, that is, harder than even Thames water is after boiling. The hardness of the former town supply in Lancashire, although often inconsiderable, was generally of the same permanent character as the old Whitehaven supply.

The hardness of water forms an objection to its use, both in cooking and washing, but the force of the objection to the Thames water for culinary purposes is much diminished by the large amount to which that water is softened by boiling. Tea is prepared in London with water which, it appears, is practically of only 5 degrees of hardness. It appears impossible to obtain any standard or test, by which the strength of an infusion of tea can be expressed in numbers, or to find any means of judging of its quality more precise than the indications of taste. On carefully comparing infusions, prepared as for family use, of an equal quantity of tea in the New River water before described, which averaged about 5 degrees of hardness, and in water of 2·4 degrees only, the observation made on several different occasions was, that the inequality in strength and flavour of the two infusions was altogether insensible to some palates. But an increase in the bitterness was more generally remarked in the soft water infusion, without enhancement of flavour. Where a preference was expressed it was in favour of the quality of the hard water infusion, but the difference between the two infusions was not considered material by any one.

Hard water is disadvantageous for making tea chiefly, it appears, by requiring the heat to be longer maintained in preparing the infusion. Tea is habitually made of excellent quality and with economy, in some families, by means of spring water of a high degree of permanent hardness, but then the infusion is continued for half an hour, and the temperature maintained near the boiling point during that period. The tea for the Greenwich pensioners is infused in a large copper, surrounded by a steam case, with water from a well in the superficial gravel of 24 degrees of hardness, of which 18·6 degrees are permanent. But in the private residences adjoining, it is found necessary to use carbonate of soda for softening, with the same water, in the absence of the efficient means of infusing described. Where any great loss of strength of the tea infusion has been observed, in passing from a soft to a harder water, it may be probably referred to the circumstance, that the mode of infusing has not been properly adapted to the hard water. The use of hard water must on this account be attended with a frequent waste of tea. The rapid process of infusion generally employed in London indicates the use of a comparatively soft water. The water to which M. Soyer gave a preference for tea-making, even over distilled water, in experiments reported to the General Board of Health, was the London deep well-water. This is usually softer than Thames water after boiling, and contains in addition a sensible quantity of carbonate of soda, to which its superiority is probably due in part. The water of the Trafalgar Square deep well has an original hardness of 5·4 degrees, which is reduced to 1·1 degree by boiling. No great objection can be taken to the use of the London water for other culinary purposes. The presence of much sulphate of lime in water makes it unsuitable for cooking vegetables, owing to the tendency of that salt to form an insoluble compound with their legumine, but this effect is insensible with Thames water.

The injury sustained in washing from the hardness of the present water supply is greatly more important, but the estimation of its amount is difficult, and involves the consideration of a variety of circumstances.

The softer the water the better is it adapted for washing with soap; the earthy salts present causing a definite and calculable loss of soap, which may be taken as amounting, with every gallon of water used in washing, to 10 grains of soap for each degree of hardness of the water. Thus, with one gallon of Thames water, at 14 degrees of hardness before boiling, the loss of soap would be 140 grains, and at 5 degrees of hardness after boiling the loss of soap would be 50 grains; or with 100 gallons of water the loss in the first case would be 32 ounces, and in the second about 11½ ounces. But such data are not alone sufficient for calculating the saving of soap effected

by the use of a soft over a hard water. For soap is used in washing not merely in quantity sufficient to soften the water, but in excess to act as a detergent. The problem is to determine how great the portion of soap lost in softening is, compared with the portion profitably used for washing in the softened water. Such data, however, are not easily obtained. In the bleaching of white goods, as scientifically pursued, soap is not made use of; the process being a series of operations in which the cloth is exposed to lime-water, carbonate of soda, chloride of lime and acid. The only practice in cotton manufactories, where quantities are exactly noted, analogous to common washing, is the soaping of dyed goods. We have found seven pounds of curd soap then used with 250 gallons of water, which is nearly 45 ounces of soap for 100 gallons of water. Now, if this water were of 14 degrees of hardness, 32 ounces more of soap would be required for softening; and of the whole 77 ounces consumed 45 ounces would be available and 32 lost, which is a sacrifice of nearly 42 per cent of the soap. With boiled Thames water of 5 degrees of hardness, $11\frac{1}{2}$ ounces would be required for softening with the 45 for washing, making $56\frac{1}{2}$ ounces together, of which $11\frac{1}{2}$ ounces or about 20 per cent of the whole soap is wasted. In the washing of woollens we find water employed with so much as $\frac{1}{80}$th part of its weight of soap, that is, 200 ounces of soap with 100 gallons of water. Here the loss of soap by using water of the two different degrees of hardness referred to, being constantly 32 and $11\frac{1}{2}$ ounces, would form a much smaller proportion of the whole soap consumed than before, namely, about 14 per cent in the one case, and 5 per cent in the other.

The maximum loss of soap by the use of Thames water employed cold would, therefore, be estimated from such data at 42 per cent of the soap employed with linens, and 14 per cent with woollens; or when the same water is softened by boiling, at 20 per cent with linens, and 5 per cent with woollens.

With woollens the loss is too small to entitle it to further consideration, particularly when it is also known that the proportion of woollen articles washed is very small with the poorer classes who frequent the public washhouses; not more, it is believed, than two or three per cent of their whole washing.

Nor is it to be supposed that, in the washing of linen, a loss of 42 per cent of soap is necessarily sustained in all cases. Carbonate of soda is generally employed by laundresses in London to soften water for washing. Indeed, this salt is used in the public washhouses in a considerably larger proportion than is necessary to precipitate the hardening salts of lime, on its own account, as a powerful detergent, particularly in the first boiling of the linen, and is not omitted although the water is soft, as with the Trafalgar Square water used in the St. Martin's public washhouses. This use of soda does

not appear to be attended by any injury to the linen, with the excellent means of wringing, by which the discoloured water is got rid of, and the abundant supply of cold water for rinsing which are provided in these establishments.

The proportion of dyed articles washed by the poor is small, and the colours are generally of a permanent kind, which resist soda. In all their washing of woollens and coloured cottons as well as white cottons, soda is in consequence equally used.

The following opinion of Mr. W. Hawes is recorded in the evidence upon this subject collected by the General Board of Health, that "Since the manufacture of crystals of soda at a very low price, and its almost universal use in washing, the waste of soap from washing in hard water has been very trifling. The quantity of soda used to soften water, as it is called, is a source of expense, but of a trifling amount." This appears to be strictly true, at least of the washing of the poorer classes, as conducted in the public washhouses.

In regard to the extraordinary injury and wear of linen from London washing often observed, and which has been ascribed to the hardness of the water, it may be remarked, that no such injury to the linen occurs in many private laundries, where hand-washing only is practised, and the use of chloride of lime and acids entirely avoided. It is most marked in the larger establishments, where much of the washing of the metropolis is conducted.

It is in the more careful washing for the middle and upper classes that the advantages of soft water become fully sensible. In the digestion of the linen in hot water, with soap and carbonate of soda, preliminary to the proper washing, the hardness of the water can only occasion a trifling loss of soda; but afterwards in the wash-tub, where soda is avoided, the earthy salts must occasion a loss of their full equivalent of soap. It is found proper also to avoid boiling any portion of the Thames water that is used in the wash-tub, or even heating that water above a certain point, for the carbonate of lime precipitates on the linen, carrying down the colouring matter of the water with it, and producing stains, which there is the greatest difficulty in afterwards removing from the linen. The colour from the water is thus indeed fixed upon the cloth, by the precipitated lime, with the tenacity of a mordant. The evil of the hardness of the water is therefore aggravated by the flood-tinge or clay-colour which the London waters often exhibit for several months in the year.

The number of gallons of water generally used with a certain weight of soap appears also to be considerably greater in London washing, than in the practice of the Lancashire bleachers, so that the waste of soap from hardness cannot fall below, but may exceed the previous estimate.

In the washing of the person the saving of soap by the use of soft water is most obvious. For baths soft water is most agreeable

and beneficial, and might contribute greatly to their more general use. Its superior efficiency to hard water in washing floors and walls, is calculated also to promote a greater cleanliness in the dwellings of all classes, both within doors and externally. While in the occasional domestic washing of linen, the smaller preparation necessary for washing in soft compared with hard water, the saving of soap which would then be sensible to its full extent, and the more easy and agreeable nature of the operation, would make a supply of soft water in a high degree desirable. The use of soda in washing would be gladly avoided by most housekeepers, owing to its injurious action on the colours of certain prints, and the permanent yellow tinge and weakness of fibre which it may occasion even in white linens when exposed to heat before the soda is entirely washed out, as in ironing. A strong desire exists to avoid its use, and where soda is avoided there is no doubt that a saving of about one-third of the soap would be made by washing linen in water entirely soft; supposing the comparison to be made with water of the ordinary hardness of the London supply, but of which one-third part was previously softened by boiling. The saving in labour would be even more considerable, if the comparison be still made between washing in soft water, and washing in hard water without the aid of soda.

2.—OF THE IMPROVEMENT OF THE PRESENT WATER SUPPLY.

A portion of the present water supply might no doubt be improved at times by submitting it to sand-filtration. The necessity for this process may be greatly diminished by the use of extensive subsiding reservoirs, such as the New River and East London Companies possess, but filtration can never be entirely superseded, being indispensable as the concluding operation of purification, to remove the vegetations and accidental impurities which may gain access to the clearest water by exposure during several days, as well as to correct original turbidity.

But the insufficiency of sand-filtration alone to clarify water which flows from clay land, particularly at the season when the water is charged with decaying vegetable matter, is obvious at times in the best filtered Thames water. Many waters of considerable softness, such as the Medway and those of the Weald of Kent, must be excluded entirely on this account, as sources of an improved supply. We doubt even whether a perfect discolouration could be commanded by filtration, either of the Lea and its higher tributaries, or of the Thames above Kingston, unless provision were made in both cases for the exclusion of flood-water.

The matters dissolved in water have been observed to diminish, in particular circumstances, after sand filtration. But any *chemical*

action which a sand-filter may exercise is soon exhausted, and it would be unsafe to calculate upon advantage from it in practice. Professor Way's observation of the power of certain clays and loams to remove much organic and saline matter from solution, is well established, but this property does not appear to admit of being applied to the rapid filtration of water in reservoirs.

Other means of improvement of the present supply have been brought before us, and engaged much of our attention, namely, the removal of carbonate of lime from water, with a portion of the organic and colouring matter, by adding to it a proper quantity of caustic lime, as proposed by Professor Clark, either in the form of lime-water, or of the dry hydrate of lime.* Carbonate of lime being held in solution by the free carbonic acid gas dissolved in water, is precipitated by boiling, which expels the gas, as already stated, and may be precipitated by removing the same gas in any other way. Accordingly caustic lime, when added to hard water in sufficient quantity to neutralize the carbonic acid, removes the solvent, and becoming at the same time carbonate of lime must precipitate together with that originally in solution. The operation of this process was first witnessed by us at the Mayfield Print-works in Lancashire, where 300,000 gallons of water are submitted to it daily, at a trifling expense, and with little trouble, but more for the purpose of discolouration than softening. A careful series of experiments made in the Laboratory, left no doubt on our minds that the means of conducting this process are certain in their results, and sufficiently simple to be left to the execution of a workman of ordinary intelligence. The precipitation of the carbonate of lime was terminated within twenty-four hours, and the water, if free from turbidity before the liming, continued in that state, but if originally turbid it remained so, and required filtration besides the liming to make it clear. The New River and Thames waters were softened in this way to an average of about $3\frac{1}{2}$ degrees of hardness, or to a lower point than by an hour's boiling.

More important trials of this process upon the large scale were afterwards witnessed by us at the Chelsea Water Works, which were conducted under the immediate superintendence of Mr. James Simpson, Jun., the Resident Engineer. The usual supply of water pumped up from the river was run into the first reservoir, in company with a small stream of milk of lime, flowing from a wooden cistern, in which the powder of slaked lime was mixed with water, and kept in suspension by stirring. The intermingled streams passed on into one of the great settling reservoirs to the extent of from 3,000,000 to 4,000,000 gallons, which is nearly a day's supply. The only precaution taken to insure the absence of any excess of caustic lime, consisted in testing the water in the settling reservoir by a drop of nitrate of silver,

* Repertory of Patent Inventions, October, 1841.

which shows if the quantity of lime required has been exceeded, by the brown colour of the precipitate then formed. After subsiding, generally for twenty-fours or longer, the water was finally passed through the ordinary sand-filters before being distributed. The degree of hardness before and after the softening process, in five such experiments, was reported to us by Mr. Simpson as follows, with the appended remarks:

THAMES WATER AT THE CHELSEA WATER-WORKS.

1851.	Degrees of Hardness.		Remarks.
	Before Liming.	After Liming.	
February 24 . .	14·0	4·5	The river was in good condition. The mixing was completed in 10 hours.
March 1 . . .	14·1	3·75	The river was in good condition. The mixing in 9¾ hours.
March 18 . . .	10·5	5	The river in flood. The flood tinge retained after liming.
March 22 . . .	11·6	4·8	Recovering from flood. Yellow flood tinge not removed.
April 17 . . .	15·5	3·6	River in an average condition.

The conclusions which were come to both by the engineer and ourselves, from these experiments, in which the operation had not the advantage of the efficient means of mixing which might be introduced where it was permanently adopted, were that the process falls easily into the routine operations of water-works, and is not attended with any peculiar difficulty on the large scale; and that the softening of Thames water in its ordinary condition by this process, to a point under 4 degrees of hardness, is perfectly practicable.

The water of the experiment of the 17th of April was analysed before and after the softening operation. The whole fixed constituents contained in one gallon of water were found to be reduced from 24·07 to 8·31 grains, and the organic matter from 2·50 to 1·60 grains; at the same time that the quantity of lime-salt present (considering it all as carbonate), was reduced from 13·65 to 2·63 grains. The softened water was clear and bright, had acquired no odour nor taste from the process, and could not be distinguished in its sensible qualities from pure spring water of equal softness.

The average cost of the application of the process in the five experiments was 1*l.* 6*s.* 2*d.* for one million gallons of water; of which almost exactly one-third was for labour, and two-thirds for lime, the latter costing 1*s.* per cwt. Mr. Simpson believes, however, that it may be reduced, and that 20*s.* for one million gallons would be a more proper general estimate. The influence which this addi-

tion to the cost might have upon the price of water, may be gathere from the following returns lately made to the General Board of Health, of the present cost to each water company of one million gallons of water:

FIRST COST OF ONE MILLION GALLONS OF WATER.

	£.	s.	d.
New River	9	17	4
East London	6	7	7½
Southwark	5	9	4
West Middlesex	16	9	7
Lambeth	15	0	6½
Chelsea	19	10	4½
Grand Junction	9	14	6¼
Kent*	17	2	10¼
Hampstead	22	5	7¼
Average (about)	£10	10	9¾

The average charge of the companies is, by the same return, about sixpence for 1000 gallons, or 25*l.* for one million gallons. The softening process would, therefore, add about 10 per cent to the original cost of the water, or 4 per cent to the price charged to the consumers.

Thames water appears always to be divested of a certain quantity of both organic and colouring matter by this process, so that its purifying influence greatly exceeds that of sand filtration. It cannot, however, be expected to exhaust the whole organic matter, and might therefore leave certain soluble sewerage products untouched. Moreover, it does not supersede the necessity for sand filtration; for the subsidence of the precipitated chalk, and the spontaneous clearing of the water by rest, after the liming, appear only to be complete when the water has been filtered beforehand, or is so bright as not to require filtration. The suspended chalk may, however, be always removed by sand filtration, and being highly crystalline and granular, it does not choke up or act injuriously upon filters. The experience of eight months at Mayfield was quite decisive, that sand filters are not injured by superadding the lime-process, but only require to be more frequently cleaned from the greater deposit on their surface.

The liming process, even when combined with filtration, proved to be unequal to remove the yellow flood-tinge of Thames water, nor did it appear to abate an objectionable taste of vegetable matter which the water also then possessed. Had the result been different the grounds for the adoption of the softening process would have been most cogent. But it seems that it is not to river-waters that this elegant and useful purifying process is most advantageously applicable.

3.—OF THE SUPPLY RECOMMENDED BY THE BOARD OF HEALTH.

For information respecting the new sources of supply, which have been proposed to the General Board of Health, the Commissioners were referred by the Board to the Hon. William Napier, with whom they accordingly communicated on the subject. They were farther supplied with the printed Reports of that gentleman's investigations, which have been communicated by him to the Board at different times, up to April 10, 1851; with the Report of the Board's Engineer, Mr. Rammell, of his examinations and gaugings of the sources recommended, dated November 9, 1850; and the Report made to the "Metropolitan Sanitary Water Company," by Mr. J. F. Bateman, C.E., with a Table exhibiting the result of the gaugings of certain streams on the proposed gathering grounds, by Mr. Joseph Quick, C.E. The Commissioners were favoured with the assistance of Mr. Napier, who accompanied them over the district of the Hindhead, to the south of Guildford, in Surrey, on the 14th and 15th of February last, when the most important spring-heads or sources were visited, and specimens of the water taken up for chemical examination.

This is a pretty well defined district, including the water shed on all sides of an elevated tract belonging to the Green Sand formation, and known as the Hindhead, over the summit level of which the post road to Portsmouth is carried for several miles. The area contains about 35 square miles, and is divided into pretty equal parts by the road. To this area we understood Mr. Napier to look for nearly three-fifths of his proposed supply, and that it was considered as rather a superior gathering ground to the larger field of the Bagshot sands, which is included in his plan, the sources in the latter quarter being similar in character, but more dispersed. A portion of the latter field, which lies near Farnham, was also visited by the Commissioners on the 13th of March, and specimens were taken of the soft water with which that town is supplied, and which is of peculiar interest, as it comes from the proposed gathering grounds.

The analysis of the Farnham water, and six selected springs from the Hindhead gave the following results:

1. ANALYSIS OF FARNHAM AND SURREY WATERS.

	Farnham.	Spring flowing into Sweet Water, Witley.	Critchmere Springs.	Vellwool, 1¼ miles from Haslemere.	The Punch-bowl, near the summit of the Hindhead.	Barford Mill-stream.	Spring at the Moors, Cosford House.
	Grains in an Imperial Gallon.						
Lime	0·6685	0·7938	0·4427	0·6801	0·6260	1·6940	6·1298
Magnesia	0·3118	0·2100	trace	trace	0·094	0·129	0·2905
Potassium	0·1939	0·1617	0·1554	0·1806	0·0429	0·1047	0 3472
Sodium	0·3927	0·4480	0·3465	0·4641	0 3030	0·3690	0·6216
Iron, alumina and phosphates	0·8930	,,	,,	,,	0·0230	0·0800	0 0·68
Sulphuric acid (SO_3)	1·0115	0·7763	0·6461	0 9730	0·4132	0·3280	1·9300
Chlorine	0·5670	0·8960	0·6617	0·5315	0·4500	0·5853	0·8484
Carbonic acid	trace	trace	trace	trace	trace	trace	trace
Silica	0·9947	0·8638	1 0045	1·2152	0·8310	0·7200	0·7287
Nitric acid	trace	,,	trace	,,	,,	,,	,,

The acids and bases found above were arranged as follows:

2. ANALYSIS OF THE FARNHAM AND SURREY WATERS.

	Farnham Water.	Spring flowing into Sweet Water, Witley.	Critchmere Springs.	Vellwool, near Haslemere.	The Punch-bowl, near the summit of the Hindhead.	Barford Mill-stream.	Spring at the Moors, Cosford House.
	Grains in an Imperial Gallon.						
Carbonate of lime	0·23	,,	,,	,,	,,	2·39	8·31
Sulphate of lime	1·31	1·32	1·07	0·86	0·59	0·40	2·48
Silicate of lime	,,	0 65	,,	0·45	1·00	,,	1·17
Nitrate of lime	trace	,,	trace	,,	,,	,,	,,
Silicate of magnesia	,,	,,	,,	,,	0·30	,,	,,
Carbonate of magnesia	0·64	0·43	traces	traces	,,	0·27	0·60
Chloride of sodium	0·93	1·14	0·88	0·87	0·74	0·94	1·40
Sulphate of soda	0·07	,,	,,	0·44	0 04	,,	0·22
Chloride of potassium	,,	0 31	0·26	,,	,,	0·03	,,
Sulphate of potassa	0·43	,,	0·03	0·40	0·09	0·20	0·77
Silica	0·99	0·45	1·00	0·93	0·10	0·72	,,
Iron, alumina and phosphates	0·88	,,	,,	,,	0·02	0·08	0·08
Organic matter	1·78	1·11	0·90	1·24	1·30	1·05	0 95
Total	7·26	5·41	4·14	5·19	4·18	6·08	15·98
Solid residue obtained on evaporation	7·33	5·31	4·37	5·17	4·34	5·65	15·75
Free carbonic acid in cub. in. at 44° F.	trace	trace	trace	trace	trace	trace	trace
Free carbonic acid, grains in the gallon	trace	trace	trace	trace	trace	trace	trace
Hardness	2·27	1·95	1·86	1·86	2·45	2·70	10·8

The Farnham water, which was collected shortly after a heavy fall of rain, was slightly turbid; all the others were pure and brilliant, and

entirely unexceptionable in point of aeration and colour. Their usual temperature when taken up was from 50° to 52°, showing that their sources are deep seated and preserve the average temperature of the whole year. Their taste betrayed no organic taint, but evinced great purity, although they appeared rather flavourless and somewhat vapid to persons habituated to the use of hard water. Their hardness proved extremely low, except that of the spring at the Moors, near Cosford House, which was of 10·8 degrees of hardness, but this is evidently a water of a different character from the others, and may be excluded from the comparison at present.

Degrees of hardness of the Surrey waters:

Farnham	2·27
Spring flowing into Sweet-water pond, Witley	1·95
Critchmere springs	1·86
Vellwool, near Haslemere	1·86
The Punch Bowl, Hindhead	2·45
Spring at Barford mill	2·70
Average hardness	2·18

These springs therefore exhibit an average hardness of little more than 2 degrees. The value of this extreme purity and softness is not diminished by the other mineral and organic constituents of the waters, which are insignificant in quantity, and really of no account. The nearly entire absence of carbonic acid from these waters, to which attention has been drawn by Mr. Napier, is perhaps their most singular chemical feature.

The question, however, arises, how far these springs represent the large supply of upwards of 20,000,000 gallons, which it is proposed to draw from this district. The visible springs are not very numerous, nor did the yield of each appear very great. The water from the largest might be carried off by a two-inch pipe. It is proposed "to lead away the deep springs only," excluding "the shallow land-springs and surface-drainage." The possibility, however, of keeping these different waters separate appeared to us extremely doubtful. The high ground consists entirely of beds of siliceous sand, rarely indurated to any extent, or converted into sandstone, which constitute enormous storing reservoirs for the springs. The springs are at all levels, and a partial outflow of water may take place at any point on the declivities, and is not determined to a certain line, either horizontal or vertical, by the occurrence of a retentive stratum, such as a bed of clay or rock, along the outcrop of which spring water might be collected. Hence the slightest cause may occasion the loss of a spring, and its reappearance at another point of lower level. From few or none of these springs can the flow be

accurately gauged, and it was not attempted by the Board's engineer, Mr. Rammell. To the gauging of the small streams or rivulets, even, Mr. Rammell observes: "an insuperable obstacle" was found "in the porous nature of the beds of the streams, which rendered all attempts to intercept or divert the whole of the flow hopeless. From this cause it was quite impracticable, either to dam up the water effectually, or to lead it along an artificial channel, laid at a less inclination, for discharge into the box (in which the water was to be measured). Most of the smaller streams have beds of perfectly clean gravel, through which, on the current being arrested, escape immediately takes place. It appeared, indeed, on close examination, that even the ordinary run of these streams is not wholly over or above the surface, but partly within the bed of the channel itself, much of the water thus passing away insensibly between the pebbles. Any attempt to dam up these streams, with a view to gauging over a weir, must have failed from the same cause."

The bottoms and sides of the springs are equally porous. A certain proportion also of the springs from which the supply is to be derived are situated in the beds of streams, and at the bottom of ponds, into which the streams expand in their course. The mode suggested to us by which these last springs could be reached, and their supply kept apart from the rivulet flowing above, was by a species of deep drainage which it was intended might carry away the water of the springs, while the surface water and ordinary field drainage would be carried off in another retentive conduit, so as to prevent the latter water from sinking into the sands, and afterwards appearing as a spring at a lower level. Into the same supplementary channel the hard springs which occasionally occur would be diverted off and prevented from mixing with the soft water of the selected springs. The supplementary channel would require to be of sufficient capacity to provide also for the escape of floods as well as the ordinary surface drainage. The extreme difficulty of keeping the two streams apart, as both must have openings everywhere to receive their respective supplies, is obvious, and appeared to us insuperable.

It appears, then, that the original plan of obtaining a great supply from the springs apart from the streams, cannot fail to be defeated by the difficulties of collecting. The water of the streams would require to be used, as appears to be intended in the modified scheme of the "Metropolitan Sanitary Water Company," which would alter considerably the character of the project. The coolness and purity of the springs would necessarily be sacrificed in part. The streams obtain, at some places, water which has been used in irrigation, and also the drainage of cultivated land. Being also soft in quality, they acquire a taint of vegetable matter with extreme facility, of which we saw instances in the ponds. The streams would of course also be subject to turbidity from floods. Their

hardness increases as they descend, from field drainage and also from hard springs, of which that at the Moors, Cosford, may be taken as an example, amounting to 10°·8 although indistinguishable in its source from a soft water spring. Dr. R. Angus Smith ascertained the hardness of three ponds in this district to be:

Frensham Pond	5·45 degrees
Little ditto	8·50
Abbott's Pond	5·25

The stream to the mill-dam at Sickle paper-mill was observed by us to be of 3·8 degrees of hardness; this is quite within the district. The Bramshot river, which drains two-thirds of the Hindhead district, leaves it at Frensham bridge, with a hardness of 5·4 degrees, the whole of which was permanent on boiling. It appeared to us that the general supply afforded from this district would not probably fall below 4 or 5 degrees of permanent hardness, if taken from the streams, which we believe to be unavoidable. This conclusion is not opposed by the recent observations of Mr. Bateman, who reports to the Metropolitan Sanitary Company respecting the Surrey gathering grounds in the following terms: –"I have not been able to discover the full quantity of water of one degree of hardness promised by the Hon. Mr. Napier in his reports to the Board of Health; but I have no hesitation in expressing my belief that a supply of at least 50 millions of gallons per day of very excellent water under 5 degrees of hardness in dry weather, and less in wet may be conveniently obtained by simple means of collection."

4.—THE QUESTION WHETHER ANY COMPARATIVE INCONVENIENCE WOULD ARISE FROM A SUPPLY OF SOFT WATER TO THE METROPOLIS, WITH THE PRESENT SYSTEM OF DISTRIBUTION.

The chief points to be considered as unfavourable to the application of soft water for the supply of a town in the peculiar conditions of the metropolis, appear to be the following.

The anti-putrescent quality of the present hard supply would be lost, and the water rendered less fit for the few days' storage which must always be had in reserve to meet the casualties of city distribution. Increased attention would therefore be necessary to insure the absence of decomposable organic matter from the water selected as the soft supply, and to protect it against subsequent organic contamination; but such difficulties are already overcome in the supply of many smaller towns, and no doubt would be successfully met, as occasion arose, on a larger scale.

A greater discolouration of the water from oxidation of the iron pipes might also be apprehended than is observed with the present

hard and alkaline supply, particularly if the water were allowed to stagnate in them.

But it is the solvent action of soft water on lead which is calculated to excite most alarm, with the general use of house-cisterns, and the universal use of service-pipes of that metal, under the present system of distribution. Of the soft spring waters from Surrey, the corrosive action on lead is remarkably small, according to our own observations, which generally accord with the conclusions of Mr. Napier on that point, with the striking exception of the water from the Punch-bowl, Hindhead, of which the power to dissolve lead proved to be rather considerable. The inactivity of the other samples we would refer more to the smallness of the quantity of dissolved oxygen which they contain, than to the absence of carbonic acid, the cause suggested by Mr. Napier. But there is little hope of a sufficient supply being obtained from these springs of this extreme degree of softness; and the harder supply from the streams of the same district would probably not differ much from the supply of Glasgow and some other large towns, where the water is always exposed to lead service-pipes, and also occasionally kept in leaden cisterns although the general supply is constant, without any apprehension of lead poisoning.

River water or spring water from the chalk strata, softened artificially to about 3 degrees of hardness, was proved by our own observations to have no dangerous action upon lead.

The experimental results obtained in a long inquiry, undertaken to illustrate the action of water in various circumstances upon lead, are not adapted for statement in this Report. The subject is one of great difficulty, and is still far from being exhausted. The most important practical conclusions which we have arrived at are the following:

Certain salts, particularly sulphates, to which a protecting effect is usually ascribed, did not appear to exercise uniformly that useful property. Some salts, on the other hand, such as chlorides, and more particularly nitrates, may increase the solvent action of water. Of all protecting actions, that of carbonate of lime, dissolved in carbonic acid, appeared to be the most considerable and surest.

The most practical, perhaps, of our observations, is the extraordinary influence remarked of the small quantity of carbonic acid, which water usually contains upon the results. This effect is fortunately to neutralize, to an extraordinary degree, the usual solvent action on lead which water exercises through the agency of the oxygen dissolved in it. The soluble oxide of lead is converted into the carbonate, which, although not absolutely insoluble, appears to be the least soluble of all the salts of lead.

Pure water did not dissolve a quantity of carbonate of lead greater than one-sixtieth of a grain to the gallon, or one part of lead in four

millions of water; while water, on the other hand, which contained already so much as six grains of oxide of lead dissolved in it to the gallon, had the quantity of metal reduced to one fifty-seventh of a grain, by free exposure to the atmosphere for twenty-four hours; the lead being deposited as carbonate of lead in consequence of the absorption of carbonic acid gas. So minute a trace of lead remaining in the water could have no possible influence on health. The quantities just stated also represent pretty closely the proportion of lead which was dissolved by water left in contact with the metal in a divided state, during a period of not more than twenty-four hours in two experiments; the water being simply distilled water in one experiment, and distilled water containing 3 per cent of its volume of carbonic acid gas in the other. The pure water became highly poisonous, but that containing carbonic acid remained safe. The lead was in the form of the lead pyrophorus, prepared from the tartrate of lead, in which the metal is in an extreme state of division, and therefore exposes an enormous surface to the water.

Carbonic acid is usually present in well, river, and lake waters, in the quantity sufficient for protection; and the immunity of such waters from lead impregnation we would ascribe often more to their carbonic acid than to the salts which they may also contain; for lead placed in distilled water which has been boiled to expel its carbonic acid, is no longer sufficiently protected by the addition of the same salts.

It is true, however, that a certain excess of carbonic acid in waters, such however as is very unusual, may give solubility to the carbonate of lead; but this solubility is not to be compared to that of carbonate of lime, the carbonate of lead requiring for solution a proportionally much larger quantity of gas.

Organic matter in a soft water is doubly dangerous, as the rapid corrosion which it occasions may be followed by solution of the lead-salt formed, when the carbonic acid is either deficient, as in rain water generally, or present above the safe proportion.

The properties of water which enable it to act at times with unusual vigour upon lead, are little understood, and seem often to arise from the accidental action of local and very limited causes, such as the presence of decaying leaves and impurities, which may only affect a small volume of water. These causes are of a kind most to be dreaded in the supply of a single residence, in which the whole volume of water might at a time assume the same dangerous composition. But such causes probably often counteract each other, when large volumes of water are mixed together, as in the supply for a town. It is at least difficult to account otherwise for the fact, that no recent and authenticated case can be cited of the health of any of the numerous towns lately supplied with soft water being affected by the use of leaden distributory tubes, although apprehensions were often entertained from the introduction of soft water, as at Boston,

in the United States, where the subject has excited much attention; and at New York since the introduction of the Croton River.

Aberdeen is supplied by water from the Dee under 1½ degrees of hardness, which is distributed by iron mains and taken into the houses by leaden service-pipes, to which leaden cisterns, generally of small dimensions, are commonly attached. The supply is constant, and amounts to about one million gallons a day. A very careful and valuable series of experiments were lately made by Dr. John Smith, Fordyce Lecturer in the University, with the view of ascertaining the action of the water on the leaden pipes by which it is conveyed. These pipes vary from 12 to 100 yards in length. In some instances no indication of the presence of lead in the water which had passed through the pipes was found; in others, however, small quantities of lead were discovered in solution. The quantities varied from one-hundredth of a grain to about one-twentieth of a grain of lead in a gallon of water. Dr. Smith concludes that less than one-twentieth of a grain of lead in the gallon of water produces no deleterious effect upon the health of those using the water for dietetical purposes, and that the lower limit of the deleterious action is between one-tenth and one-twentieth of a grain of lead to the gallon of water. Here then is a population, it might be supposed, constantly on the verge of danger from lead poison, but in reply to our inquiries upon the subject we are assured by Dr. Dyce, the eminent physician of Aberdeen, that during a period of seventeen years he has never known an instance of illness from this cause. He adds in his letter: "I have mentioned the circumstance to several of my colleagues, and they all decidedly say that such a complaint is wholly unknown to them." From Whitehaven also, where water of the same extreme softness has been in use for the last six months, we learn that no case of lead poisoning had been seen or heard of by the medical practitioners of the town which could be attributed to the use of the water. No cisterns however are used there, nor in any of the other towns where soft water has lately been introduced, as they may be dispensed with on the system of constant supply, which appears always to have been adopted with the soft water.

We are disposed, therefore, to conclude that the danger from lead in town supplies of water has been over-rated; and that with a supply from the Water Companies, not less frequent than daily, no danger is to be apprehended from the use of the present distributory apparatus, with any supply of moderately soft water which the metropolis is likely to obtain.

5.—OF THE WATER PROPOSED TO BE SUPPLIED FROM WATFORD.

The water, which it is proposed to bring from the neighbourhood of Watford for the supply of the metropolis, claims consideration as being entirely spring-water, and has a peculiar scientific interest as representing the pure primitive basis of the river water which is at present consumed. A supply of water of the same description is also offered from the south side of the river, to be derived from the chalk strata upon the line of the South-Eastern Railway, and the quantity attainable on either side is said to be so considerable as to exceed the actual requirements of the metropolis. Of the chalk district, which surrounds London on all sides, and covers an area of not less than 3000 square miles, the upper strata appear to be charged with water to a height of several hundred feet above the level of the sea. This water issues again in numerous natural springs, or may be reached by moderate boring. The daily yield of single springs or of artificial wells in some parts of this district is remarkable for its quantity, often amounting to 300,000 gallons, and occasionally rising to 1,000,000 gallons and upwards; a copiousness of flow which is referred to the chalk rock being highly pervious to water, from its fractured and cavernous state. This chalk spring-water is not to be confounded with the water of the deep wells of London, although the latter are carried into the chalk strata below the clay, but differs as completely in composition from the latter as any two waters can well do. Nor does any evidence exist of a relation or dependence of the London deep wells upon the water of the Chalk districts; nor reason to infer that the yield of the latter would be restricted within the narrow limits of the former. Indeed, all grounds for comparison of the two waters will disappear if it is true, as many well-informed persons believe, that the deep wells of London draw their supplies chiefly from the sands under the blue clay and above the chalk, the water of which sands appears to flood the upper beds of the chalk. The superposition of the thick mass of strata, which form the London clay, certainly alters considerably the condition of the chalk below it, and renders it no longer comparable with the water-bearing strata of chalk in Hertfordshire and Kent, which are not so covered, and are situated above the level of the sea. The whole original supply of the New River Company from the Chadwell and Amwell springs, was water of the kind under consideration, and a very sensible proportion of the present large supply of that company is still spring or well water of the same nature.

The proposals of the "London (Watford) Spring Water Company" extend only to a daily supply of about 8,000,000 gallons. But the

area of land sloping towards Watford, and consisting for the most part of chalk hills, embraces more than 1200 square miles, and is estimated by Mr. Homersham, the Engineer of the Company, as equal to a daily supply of 408,000,000 gallons; the quantity of water which reaches the lower fissures of the chalk being calculated at one-half of the rain-fall.

A well sunk in Bushey Meadows, in 1840, when this source of supply was first recommended by Mr. R. Stephenson, has been found capable of yielding by pumping 1,800,000, or nearly two million gallons per day. This well is 12 feet 6 inches in diameter at the bottom, and 34 feet deep, with 4 small bore-holes, 5 inches in diameter descending 130 feet below the surface of the ground. The surface of the water in this well, when lowered to its greatest depth by pumping, is said still to stand 136 feet above Trinity high-water mark. It is proposed to obtain the remaining portion of the water required by this Company by sinking other wells in Bushey Meadows, or by driving adits through the chalk formation under the meadows. The site of the experimental well referred to is on the banks of the Colne, within three-quarters of a mile of the town of Watford, and distant, in a north-westerly direction, about fourteen miles from Cumberland Gate, Hyde Park. The water of this well was not in a suitable state for examination when visited in February last, owing to the access of surface water. The supply of water for examination was, therefore, taken from other wells in this district, namely in the town of Watford, at Batchworth, near Watford, and at Redbourn, near St. Alban's. Although the extreme distance of these sources from each other is more than eight miles, the results of their analysis are quite similar, and also correspond closely with anterior analyses of the well in Bushey Meadows.

I. ANALYSIS OF CHALK SPRING WATERS FROM WATFORD.

	Batchworth Water.	Redbourn Water.
	Grains in the Imperial Gallon.	
Lime	9·0330	10·3792
Magnesia	0·3587	0·2580
Potassium	0·4746	0·3400
Sodium	0·8246	0·3340
Sulphuric acid	0·9471	0·3778
Chlorine	0·6142	0·6360
Carbonic acid	15·0220	14·3640
Silica	1·5900	1·1600
Nitric acid	0·1540	0·7000

2. ANALYSIS OF CHALK SPRING WATERS FROM WATFORD.

	Batchworth Water.	Redbourn Water.
	Grains in an Imperial Gallon.	
Carbonate of lime	16·13	17·94
Sulphate of lime	,,	0·11
Nitrate of lime	0·23	1·06
Carbonate of magnesia	0·75	0·53
Chloride of sodium	1·01	0·85
Sulphate of soda	1·31	,,
Chloride of potassium	,,	0·25
Sulphate of potassa	0·44	0·58
Carbonate of potassa	0·48	,,
Silica	1·59	1·16
Organic matter	1·26	,,
Total	23·20	22·48
Residue obtained on evaporation	22·97	21·63
Free carbonic acid in cubic inches at 44° F.	15·3	12·48
Free carbonic acid, grains in the gallon	7·6	6·24
Suspended matter	,,	,,
Hardness observed	$18^{0}{\cdot}1$	$17^{0}{\cdot}8$

On comparing the Watford spring water with the New River water and Thames water as supplied by the Water Companies, a considerable similarity is observed in the character of their saline constituents. The lime is in larger quantity in the spring water, but then it is nearly if not entirely in the state of carbonate. The earthy sulphates, which give rise to permanent hardness, are almost entirely absent from the spring water. The general character of this supply may be farther described as follows:—

1. The spring water contains no matter in suspension to cause turbidity or colour; its clearness and brilliancy are unexceptionable.

2. It possesses a desirable coolness, having at all seasons a temperature between 50° and 52°.

3. The amount of organic matter it contains is inconsiderable, and of a kind which appears to be incapable of undergoing putrefactive decomposition, so that it may be safely disregarded.

4. The salts which it contains would not interfere with its use as a beverage. It is indeed a choice water for drinking.

5. The great and obvious objection to the chalk spring water is its hardness, which, when the water is first drawn, is uniformly very nearly 18 degrees, or 4 degrees harder than the present metropolitan supply. The weight to be assigned to this objection, however, appears to be much reduced by the following considerations.

A portion of the carbonate of lime, which occasions the hardness, is deposited from this water when exposed to the atmosphere, with

remarkable facility, from the escape of carbonic acid gas. According to the statement of Mr. Homersham, which we have no reason to doubt, this water, when collected and allowed to remain for a few days in reservoirs suitable for distribution, becomes as soft or softer than Thames water. The Redbourn water was observed by us to soften by exposure to air for forty-eight hours in a shallow vessel, without any sensible evaporation, from 17°·8 to 14°, a visible crystalline deposit of carbonate of lime appearing at the same time. This softening may go on to a greater extent than is generally supposed, for in an extreme case where the Redbourn water was exposed to air in a shallow glass basin for eight days, and one-fifth part of the whole water was lost by evaporation, the remaining four-fifths exhibited a reduced hardness of only 9·1 degrees. In the course of an investigation of the spontaneous softening of chalk waters by exposure, a subject which appeared to us of some importance, it was discovered that these waters may be softened in a few minutes by means of agitation in air, to about 13·5 degrees, provided a quantity of the precipitated carbonate of lime be previously mixed with the water. The crystalline grains of chalk appear to promote the separation of carbonate of lime from the water; the grains no doubt increasing in size by an accession of matter. Siliceous sand agitated in contact with the hard water did not produce the same effect.

The chalk spring-water is softened very fully, as might be expected, by boiling. The Batchworth water merely heated to the point of ebullition, fell to 12 degrees of hardness; by five minutes' boiling to 5·6 degrees; by fifteen minutes to 4 degrees; by thirty minutes to 2·8 degrees, and by an hour's boiling to 2·6 degrees. The final result almost coincides with the effect of boiling upon a solution of pure carbonate of lime in distilled water containing carbonic acid gas, which was reduced to 2·4 degrees. New River water, it will be remembered, has its softening limit by boiling at 4·1 degrees, and Thames water at 5·5 degrees. In all applications of water, therefore, where it is boiled, no loss, but on the contrary a small gain would be experienced, by substituting the chalk spring-water of Hertfordshire for the present supply.

The high degree of hardness of the chalk spring waters is also greatly redeemed by their peculiar adaptation to the softening process. The Batchworth spring was thus reduced to 2·6 degrees of hardness, when lime-water was used, and to 2·8 degrees by means of the solid hydrate of lime; the Redbourn spring to 2·5 and 2·6 degrees. Such is the degree of softness, therefore, at which this supply is attainable. From the extreme purity of the water the precipitated chalk falls entirely colourless, and, indeed, from its finely levigated condition might be sold as whitening. The precipitation appeared to be completed within twelve hours, and was so perfect that no filtration of the water was necessary. The water retained all its

original brightness and transparency, and acquired no flavour or other property by which it could he distinguished from the equally soft waters supplied by nature. The experience obtained by us of this softened water as a beverage for some weeks was confirmatory of the statements that the palate becomes gradually reconciled to the impression of a soft and pure water.

It is a valuable property of the chalk spring-water, that in practice it may be softened fully or partially with the same facility, or to any degree desired; the precipitate falling quickly and completely in every case, and leaving the supernatant water clear and colourless.

Respecting the supply of chalk spring-water from the south side of the Thames, our information is principally derived from a Report by Mr. Peter W. Barlow, on the supply of water to be obtained from the North Kent district, addressed to the Chairman and Directors of the South-Eastern Railway Company, to which is added a Geological Report on the district by Professor Ansted, with analyses of the waters by Professor Brande.* The district directly available extends about 20 miles along the North Kent Railway, between Blackheath and Higham, and includes according to Mr. Ansted about 180 square miles of country, consisting of chalk beds of great thickness, reposing upon the Wealden clay, which is very retentive of water. The chalk is said to be of a somewhat open texture, the surface broken by numerous fissures, and the mass of the rock to have many joints and also faults. Mr. Ansted found by experiment that chalk in this state, and when fully saturated, contains about two gallons of water in each cubic foot of chalk. That the district is composed of highly pervious strata appears from the fact, remarked by Mr. Barlow, that the whole rain which falls upon it does not produce any surface stream, but appears to escape chiefly by subterraneous channels into the Thames. The water issues again at some points in great abundance. One group of springs which occurs near Northfleet Station, were found by Mr. Barlow to discharge from 7 to 9 million gallons a-day; and the whole supply, which may be conveniently intercepted by adits, or numerous bores into the chalk along the line of the railway, is roughly estimated by Mr. Ansted at 60 million gallons daily, and the supply, at a moderate depth, considered to be practically inexhaustible. It does not fall within our province to discuss engineering estimates for works, or even calculations of quantity, but the interest of the information, and its trustworthiness as coming from Mr. Barlow, excuse a reference to the outlay involved in a scheme of so much novelty. The estimate for bringing the water to the terminus at the Bricklayers' Arms, for the supply of London on the south side of the Thames, is £150,000, which includes the cost of a heading, or small tunnel, driven under the line of railway, at or about the level of low-water mark, with borings every half mile; and no liability

* Printed by James Truscott, Nelson Square, London, 1850.

whatever is incurred to compensate land-owners for existing rights to water.

The good quality as well as the abundance of the water from the chalk has been proved in every case, according to Mr. Barlow, where the water has been required by the Railway Company, and seven of their locomotive stations are thus supplied. The water of the southern chalk districts is also found suitable for town use, as at Gravesend, Folkestone, Dover, Brighton, Lewes, Portsmouth, Ramsgate, Deal, Canterbury, Arundel and Winchester.

The town-supply of Gravesend was taken for analysis to illustrate the chemical qualities of the chalk spring-water of Kent. The sample was perfectly bright and colourless, and proved to be very similar in composition to the Hertfordshire waters.

1. ANALYSIS OF WATER FROM GRAVESEND WATER-WORKS.

	Grains in an Imperial Gallon.
Lime	10·5630
Magnesia	0·1334
Potassium	0·5900
Sodium	0·9040
Iron, alumina and phosphates	0·2557
Sulphuric acid (SO_3)	0·5925
Chlorine	1·1775
Carbonic acid	14·7900
Silica	1·0150

2. ANALYSIS OF WATER FROM GRAVESEND WATER-WORKS.

	Grains in an Imperial Gallon.
Carbonate of lime	18·86
Sulphate of lime	,,
Carbonate of magnesia	0·28
Chloride of sodium	1·94
Sulphate of soda	0·74
Sulphate of potassa	0·38
Silicate of potassa	0·65
Silica	0·69
Iron, alumina and phosphates	0·26
Organic matter	0·73
	24·53
Residue obtained on evaporation	24·54
Free carbonic acid in cubic inches	13·31
Free carbonic acid, grains in the gallon	6·5
Suspended matter	,,
Hardness	19·56

The hardness of this water was reduced, by boiling, from 19·5 degrees to 3·2 degrees. The water from a newly-opened well in the chalk at the Railway Station, Gravesend, fell by boiling from

21·3 to 2·8 degrees. These waters admit also of an equally high degree of softening by the lime-process, as the Hertfordshire chalk springs, to which they appear to be in every respect similar and equivalent in value.

6.—OF THE PROPERTIES TO BE PREFERRED IN THE WATER SELECTED FOR THE SUPPLY OF THE METROPOLIS.

The properties which we would esteem of most value in water to be supplied to the metropolis are:

1. Freedom from putrescible organic matter.
2. Freedom from constant, or even occasional discolouration by clay and vegetable matter, with perfect brightness and clearness.
3. Softness.
4. Coolness.

The nearer the sources of rivers are approached, the more fully are they likely to possess the two first requirements, freedom from organic impregnations and from colour. The New River water may be instanced as offering the most favourable exhibition of the good qualities possessed by any portion of the present metropolitan supply. Taken from the Lea, above Ware, this water has a superiority, which is generally admitted, over the supplies from the Thames, which would no doubt be further increased by the removal of the Hertford drainage, by recourse for additional water to the higher tributaries of the Lea, as proposed by the River Lea Trustees, and by shortening the channel of the New River by about twelve miles, which is also contemplated. But it is only by proceeding to the actual sources of rivers, that the water of the latter can be protected completely from field and house drainage. Hence the general disposition to abandon rivers, as sources of town supply, and to allow them to remain, as they must always be, the natural and indispensable channels of drainage, and the occasional means of fertilizing irrigation.

The contemplated improvements of the New River appear to embody a portion of the comprehensive scheme of Captain Vetch, who, after a careful survey undertaken by direction of the late Metropolitan Board of Sewers, recommended the appropriation of the unobjectionable chalk streams on either side of the Thames as the future sources of supply; abandoning the River itself for its purer tributaries, and giving a preference to those streams which enter the Thames below London, so as to retain the volume, and scouring power, and with these the salubrity of the upper part of the river unimpaired. To this last object Captain Vetch attached great importance with reference to the prospective increase of the metropolis, which he reminds us has doubled its population within forty years. The eminent engineer, Mr. Telford, to whom the question of the metro-

politan supply was referred by Government after the Water Inquiry and Report in 1828, had previously recommended, after a prolonged investigation, to bring the water from the River Verulam, near Watford, for the supply of the districts on the north side of the Thames, and from the River Wandle for the supply of the districts on the south side. In 1840, a further step was taken in the same direction, the "London and Westminster Water Works Company" being at that time established for supplying the metropolis with water from the springs in the chalk, near Watford. This Company proceeded upon a Report by Mr. Robert Stephenson, which appears to be founded on sound scientific principles and great local knowledge. Mr. Stephenson concludes, that the necessary supply for London could be obtained and conveyed from that source, and speaks in the highest terms of its quality. He expresses his surprise, that with the exception of the abortive project to obtain water by perforating the London clay, all preceding proposals, "including Mr. Telford's, should have contemplated using the water of streams which are all subject to be affected by the surface-drainage of a more or less extensive tract of country, and consequently only a very few degrees better than that already in use."

Our great engineers have thus returned, step by step, to the original idea of Sir Hugh Middleton, who had recourse to the pure fountain-heads of Hertfordshire for the supply first brought by him to London by the New River; acting, no doubt, upon the traditions of antiquity and the example of the Roman hydraulic works, which are still unrivalled. Of the two divisions of Hertfordshire, which are drained respectively by the Colne and the Lea, the former, or north-western district containing Watford, appears to exceed, in available water sources, the latter, or north-eastern district, the field which is already occupied by the New River Company.

The inhabitants of London appear to have within their reach, in these chalk strata, a supply of water, which is asserted, on good authority, to be inexhaustible, and which may be considered as everywhere of an uniform composition and quality. The rain falling upon the downs and elevated ridges is rapidly absorbed by the soil, and enters the chalk beds, through the porous and amply aerated channels of which it circulates, much of it probably for centuries, before subsiding to the lower level of the valley springs. Hence a full decomposition of any alterable organic matter, and the assumption by the water of a constant and uniform character.

The chalk spring-water unites the greater number of the desirable qualities already enumerated. It contains absolutely nothing of organic origin capable of further alteration or decomposition, and is therefore wholly unobjectionable, on the ground of organic constituents. Its clearness and brilliancy also appear perfect, from the complete absence of suspended matter, and are highly attractive. Possessing

at all seasons the mean temperature of the year, the same water has an agreeable coolness and freshness, which might certainly be preserved in a great degree by proper means of conveyance and distribution. The only other quality desired in a town supply was softness. The chalk spring-water is not naturally a soft water. In this respect, it is inferior to the present supply, being one-fourth harder; but it will be remembered, that the hardness of both is principally of the temporary kind, and that, after boiling, the advantage is with the spring water. It is, however, in the facility and completeness of the removal of this hardness, that the superiority of the spring over the river water is most apparent. The softening operation, by the use of lime, is applicable in all seasons to the spring water, which indeed adapts itself with singular felicity to that process, the carbonate of lime always precipitating with rapidity, and so completely as not to create a necessity for filtration. The chalk spring waters can thus be commanded with certainty, under three degrees of hardness, which is probably the extreme limit attainable anywhere in England for a great supply. The lower price of lime in the chalk districts, and the reduction in the labour of mixing, must also bring the cost of the process considerably within the estimate formed at the Chelsea Works, and would not, we believe, form a greater addition than a sum equal to two per cent upon the present price of water. This is without allowing anything to be obtained in return for the precipitated chalk, which would certainly have some market value.

The chalk spring-water after being softened is an extremely pure water. It appears to be considerably superior even to the soft water from the streams of the Surrey Sands. The chalk water alone is uniform in its excellence at all times, the sources of it lying beyond the influence of weather or season. In the judgment of the Commissioners, this softened chalk water is entitled, from its chemical quality, to a preference over all others for the future supply of the Metropolis.

It is no longer possible to disregard the chemical means of removing hardness, or to represent them as impracticable on a great scale; they place the question of water-supply upon an entirely new footing. Efficient as these means already are, we confidently look to their farther improvement, when the large results of practice come under the eye of the engineer and scientific observer. Another mode of partial softening, without the consumption of lime or any other material, by the united action of air and granular carbonate of lime upon the carbonated water, has been already referred to, which may probably soon have its powers tested, either as an auxiliary to Dr. Clark's process, or as a substitute for that process, when a less considerable softening is required.

An incidental advantage of artificial softening for the London

supply is, that the change in quality can be graduated to any point desired. It may be advisable to furnish the water at first with a hardness of 5 or 6 degrees, which is considerably above the point at which any action upon lead need be apprehended, and therefore compatible with the cistern-storage of water, which the actual system of supply requires. The circumstance that this residuary hardness after liming yields readily to boiling, combined with the absence from the spring water of all colouring impurity would insure that water a decided preference for washing and most other applications, even were it no further softened. But it might be reduced we believe with perfect safety to 3 degrees of hardness, as soon as the taste and habits of the consumers were accommodated to so soft a water. To obtain the full advantage of its great coolness in the hot summer months, the supply would require to be constant, and the house-pipe to communicate directly with the main. But although this change is desirable on other important grounds, it is not indispensable to the first introduction of the softened chalk spring-water.

The water recommended appears to approach most closely to the standard of all that is excellent in a town supply, and is worthy of the greatest efforts and grandest works to procure and convey it. But the sources are near at hand, and the water is attainable without difficulty or great expense. With such a noble application of the chalk spring-water in view, as the supply of the metropolis, it would be a desecration to permit that water to be wasted on other uses, and most impolitic to allow the possession of it to pass into private hands. It is our deliberate opinion, which we would enforce in the strongest terms, that the much desired and most necessary improvement in quality, of the London water, is associated with these sources of supply, and will depend upon their proper application to the uses of the Public.

We have the honour to be, Sir,

Your very obedient Servants,

THOMAS GRAHAM.
W. A. MILLER.
A. W. HOFMANN.

London, June 17, 1851.

To the Right Hon. Sir GEORGE GREY, Bart.,
Her Majesty's principal Secretary of State for the
Home Department.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1851.

A.

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